OXIDATIVE POLYMERISATION OF CALCIUM LIGNINSULPHONATE

A thesis presented for the degree of Masters of Science in Chemistry in the University of Canterbury, Christchurch, New Zealand.

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CONTENTS

ABSTRACT

The study of the formation of ligninsulphonate gels of low concentrations and catalysed by ferric chloride was made with particular reference to their use as groutings for ground electrodes for the New Zealand Electricity Department. The physical, electrical and chemical properties of these gels were investigated and "optimal" gels of least cost mixtures, of satisfactory performance were formulated. Among other additives tested, copper chloride was selected as the best substitute for ferric chloride as a promoter to give better gels.

A dimerisation-condensation mechanism as the primary mechanism for gelation of calcium ligninsulphonate is not supported by evidence collected here and an alternative, oxidative reaction for the polymerisation is established. Transition metal chlorides with favourable electron-transfer properties strongly catalyse the redox process and hydrogen ions released from hydrolysis of these salts contribute to the promotion of the gelation as an essential reagent. Attempts were made to utilise the understanding of the chemical properties process of gelation to help improve on the "optimal" gels.

CHAPTER I

INTRODUCTION

1.1 The Problem

A study of the polymerisation of calcium ligninsulphonate was initiated after an approach by the New Zealand Electricity Department (N.Z.E.D.) to look at the optimum concentrations of the reactants of the process which they were investigating as a possible conductive "grouting" to be injected around the bases of high tension power pylons especially in shingly ground with low electrical conductance. In dry soil conditions, transmission line tower footing resistances of 30 to 200 ohms are found and such high values are undesirable for saftey and operational reasons.[1]

Normally rods driven down 100 ft or more close to the tower have been found most effective in reducing the footing resistance. However a more satisfactory technique was being sought by the N.Z.E.D., the most attractive of which was the recent use of the ligninsulphonate gels as ground electrodes. Some tentative work has already been started on testing the gel electrode by the N.Z.E.D. at Christchurch Airport and further studies were being sought in the development of an optimal ligninsulphonate gel. The factors which were believed to be important by the N.Z.E.D. which led to the selection of the optimum chemical concentrations and composition of the gel and which would be considered in this thesis are:

1. Cost
2. Gelation times
3. Desirable chemical additives
4. Physical, chemical and electrical stability.

Leaching effects and the effects of high current are also important but would be outside the scope of this work.

1.2 Ligninsulphonate Gels

The chemical gel electrode was first developed by the Chuba Electric Power Co[2] in 1970 by the addition of sodium dichromate to calcium ligninsulphonate which on gelation, binds the soil together in a solid yet flexible mass. The gel or resin is a polymer with an irregular net structure which enables it to occulude water in large quantities within a network of fine pipes all mutually connected. This structure is conductive and because the occuluded water is contained in ultra-fine pipes, prevents excessive leaching which would otherwise destroy the conductivity of the structure. The inorganic salts from the dichromate oxidant and from added catalysing salts also contribute to the conductivity.

Initial field tests by the Japanese with the ligninsulphonate gel has so far proved encouraging in terms of the following properties:

(1) It performed satisfactorily over a wide spectrum of soil conditions. It was far superior to other

chemical agents at reducing resistance and maintaining the effect with time. Ligninsulphonate electrodes are typically 35% lower in resistance three years after their construction.

(2) It is resistant to transients and stable to the effects of high current.

(3) It is very resistant to dissolution by ground water and hence has longevity in the ground.

(4) Its corrosivity is negligible.

(5) It is not poisonous.

(6) Unlike other chemical agents as bentonite and copper ferrocyanide gel, the lignin gel is easy to use and does not deteriorate with age.

(7) What makes the ligninsulphonate gel electrode so attractive over all existing methods of reducing tower footing resistance is the economics in that it has been estimated that it costs from one-fifth to one third of the cost of a standard installation using driven ground rods which is the prevalent method. The ligninsulphonate reducer is plentiful and relatively inexpensive.

1.3 Calcium Ligninsulphonate (as Discon.) and Lignin.

Commercial calcium ligninsulphonate is a by-product of the wood and cellulose industry, the largest source is the pulp and paper industry and only lately was the potential use of commercial lignin begun to be developed.

The properties of lignin has already been extensively investigated.[3] Lignin is after cellulose, the principal

constituent of the woody structure of higher plants functioning in nature to act as a cement agent to bind the matrix of cellulose fibers together into a rigid structure. Its exact chemical structure in wood substance is not yet known but much is known about the structure of isolated lignins.

Lignin is not a single polymer formed from a single type of monomer and structurally it is thought of as a complex and variable branched chain polymer based on phenylpropane (C_6-C_3) units which bear several functional groupings such as, methoxyl, carbonyl, aliphatic and aromatic hydroxyl groups, phenolic hydroxyl, ethers and thioalcohols. It is now reasonably clear that at least twenty guaiacylpropane units must be linked together in order to represent most of a typical lignin molecule. The phenylpropane units in lignin are linked by aliphatic and aromatic carbon bonds and ether bonds, and it is generally believed that they are linked randomly. A good working model of the lignin structure is represented by a plausible structure for coniferous lignin as illustrated in fig. 1.

The composition of commercial lignin is variable and is dependent on both method of isolation and primarily on source of wood. For example from the elemental analysis and methoxyl content, the empirical formula for coniferous lignin, based on the phenylpropane unit is $C_9H_{8.83}O_{2.37}(OCH_3)_{0.96}$ with a molecular weight of 184 for the average unit (monomer). It is assumed that coniferous lignin contains about 14% p-hydroxyphenylpropane

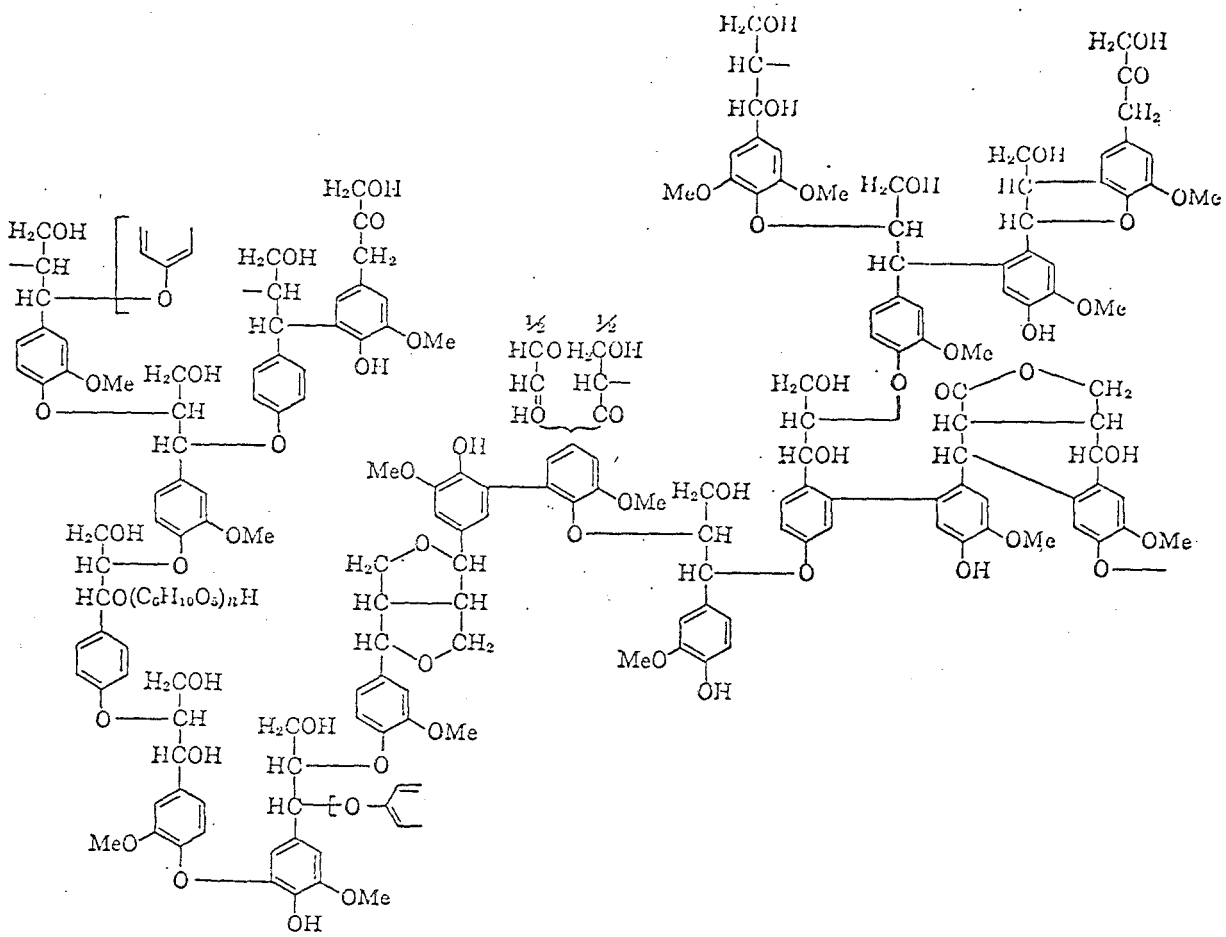


FIGURE 1: REPRESENTATIVE STRUCTURE OF CONIFEROUS LIGNIN.

units, 7% syringylpropane units and 79% guaiacylpropane units. This accounts for the presence of slightly less than one methoxyl groups for an "average" phenylpropane unit in the lignin polymer. The average weight is believed to be over 10,000. Similarly, the empirical formula for a phenylpropane unit in deciduous lignin is calculated to be $C_9H_{8.9}O_{3.0}(OCH_3)_{1.45}$ with a molecular weight of about 210 for the average unit. It appears that there are about three syringylpropane units for every two guaiacylpropane units in deciduous lignin polymers and that the average molecular weight of the deciduous lignin probably does not exceed 5000.

The polydispersity of soluble lignin is seen in the concept[11] that lignin exist in the wood as a network of short linear chains, cross-linked in a variety of ways to give an infinite three dimensional structure. During the pulping process the network is broken down by chemical agents which breaks covalent bonds and reduce the network to fragments of various sizes.

During the cooking process, hydrophilic groups such as $-SO_3^-$ or $-COO^-$ are generated on the network and on the fragments. These groups convey two useful properties in that they render the lignin sulphonate polymer water-soluble and also contribute to electrical conductivity of its solutions. The sulphonate group retained during gelation of the polymer (see next section) enables the gel formed to show the strong hydrophilic properties of the original polyelectrolyte and is therefore responsible

for the gel to retain the water which was in the starting solution.[4]

1.4 Oxidative Polymerisation of Calcium Ligninsulphonate

Since ligninsulphonates are known to contain a large number of distinct functional groups, it is no wonder that the polymer is capable of undergoing a vast number of reactions. One of these in relation to our studies is the polymerisation of ligninsulphonate with sodium dichromate[5,6]. The factors which affect the polymerisation rate have been established and these include:

(1) Nature of the ligninsulphonate resulting from different cations e.g. ammonium, calcium, sodium etc[7] - the ammonium based gelation mixture gave the fastest setting times but its gel formed is a little less stable than the calcium product; the stabilities of the sodium ligninsulphonate are very poor.

(2) The concentration or density of ligninsulphonate[7,8] - for a fixed ligninsulphonate: dichromate ratio with zero activators, the gelling time increase as the concentration of ligninsulphonate. With addition of ferric chloride as activator, the gelling time is reduced and varies in a complex manner as described in Chapter IV.

(3) The concentration of dichromate as a function of ligninsulphonate: dichromate ratio - A minimum

amount of chromic acid proportionate to the concentration of ligninsulphonate is necessary for gelation[8,9] while from the results in Chapter IV gelation is speeded with increase of dichromate but up to a certain amount when large excess of the oxidant would lead to its deterioration and inhibition.

(4) The addition of activators (e.g. metal chloride salts) or retarders (e.g. boric acid) - when a small quantity of salts are added, copper chloride causes the fastest gelation, aluminium is next and ferric chloride the slowest. For larger quantities, iron chloride additives increase the speed dramatically and can attain a gelation time of two or three minutes.[8] The relative acceleration of these salts was studied in greater detail later in Chapter V. The gelation of a ligninsulphonate-dichromate mixture can be greatly slowed by addition of comparatively large amounts of borax or boric acid without detriment to the gel.[10] Inert solids tend to speed up gelation slightly.[5]

(5) PH of gelling mixture - In general[5], alkalis retard while neutral salts and acids accelerate the setting. The polymerisation proceed most readily at an optimum pH of between 3.5 to 4.5.[4] The reaction is slowed down considerably at higher pH and at approximately one normal sulphuric acid, the solution no longer gels indicating a

repression of the reaction by strong acid.

(6) Temperature - the rate of gelation is increased with rise of temperature,[5] e.g. the setting time of a given dichromate - ligninsulphonate mixture at 50°F is approximately double[7] that for the same mixture at 70°F. At temperatures above 40°C however, the polymerisation is inhibited[4] probably by the general oxidative reactions of the polymer.

(7) Molecular weight of ligninsulphonate - Hayashi[11,12] found that the minimum molecular weight for ligin-sulphonate to gel was 2,900 but in this work, gelation was found to occur readily with average molecular weight of 654.0.

1.5 Mechanism of Polymerization of Ligninsulphonate by Dichromate

Over the years since Haage first discovered the gelation of lignosulphonate by dichromate in 1908, the gelling reaction has been investigated largely in connection with its potential use as soil stabilisers and other engineering uses. It was only recently that some considerable work on the kinetics of the polymerisation reaction was carried out in Japan mainly by Hayashi and workers[13,4].

Twining[5] first described the polymerisation as involving the formation of some sort of chromic complex with the lignosulphonate containing variable amounts of other

anions and water.

Aaltio and Roschier[14] suggested that the oxidation with dichromate removes sulphonate groups and at the same time carboxyl groups are formed, to which the trivalent chromium coordinates together with other oxygen containing groups in the molecule. Unfortunately no experimental evidence was produced to support this view.

Julian C. Smith[15] also proposed that the chromium coordinates with oxygen atoms in sulphite wastes containing ligninsulphonate, possibly after oxidation of calcium ligninsulphonate to form carboxylic acid groups. The active sites of polymerisation were suggested[10] to be the phenolic groups which react with the chromium to form large macromolecules. These phenolic groups are formed by an oxidation of a plurity of aromatic groups contained in the complex lignin molecule.

James and Tice[16] were able to remove almost all of the chromium from a gel by digestion with ethylenediaminetetraacetic acid and on the basis of their studies, they concluded that the gel is composed of polymerized lignosulphonate and hydroxylated chromic species, a small proportion of which are firmly bound. The ligninsulphonate is presumably polymerised by phenolate coupling reactions, and at the same time carboxyl groups are formed. The gel may be described as consisting of high-molecular-weight microgel units of basic chromic ligninsulphonate linked together through carboxyl groups

by trivalent chromium atoms.

Hayashi[13] and in conjunction with other workers studied the gelling reaction by means of rheological, conductometric, spectrometric and a host of analytical methods and making extensive use of model compounds. From these results, a fairly detailed picture of the mechanism emerged though by no means complete.

It has been proved beyond doubt[12,17] that one of the active sites for polymerisation is a specific type of phenolic group and was identified as the pendent catechol group. These catechol groups on the lignin molecule are produced during the sulphite pulping by demethylation[18] of pendent guaiacyl groups via a slow general hydrolytic reaction of phenolic ethers. Alternatively they are also generated[19] simultaneously during the gelling reaction by the action of dichromate.

Rheological, pH and conductance data showed that the gelling reaction consists of three well defined stages.[4,13] First the dichromate ion complexes with the catechol groups on the lignosulphonate, pictured as a micro-gel[20]. Then crosslinking takes place between the chrome-complexed sites and finally when the density of crosslinking is high enough, the solution gels, Fig. 2.

The gel is not held together by electrostatic bonds between chromic ion and carboxylic residue produced by oxidation as suggested by earlier workers. The chelation between the pendent catechol groups and chromate ions

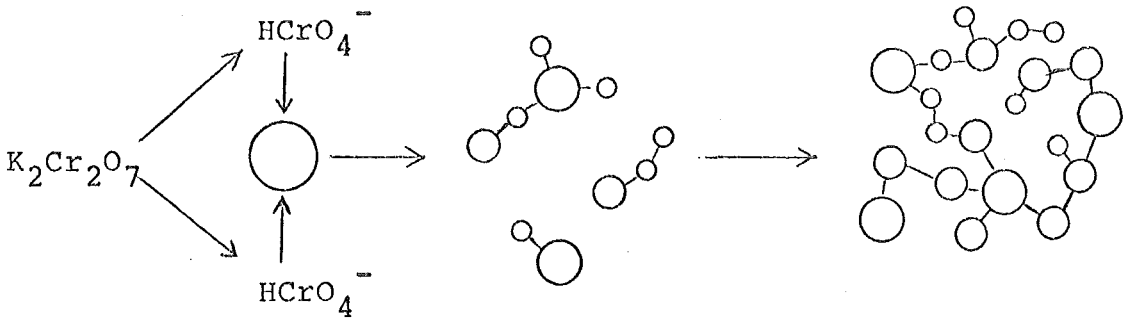


FIGURE 2: Reaction gelling scheme of ligninsulphonate with dichromate.

produce cyclic chromate esters which on interacting together dimerises[12] or polymerises by condensation through an oxygen atom in stage 2 and thereby producing intermolecular crosslinks of oxygene bridges. James and Tice[16] showed that the crosslinks involved coordination with the chromium and the valency[21] of the chromium bound in the gel and was examined through perchromate reaction with hydrogen peroxide and through E.S.R. method. Both results indicated that the bonded chromium is the chromium (VI) species which meant that the linkages also involve catechol-chromate bondings as shown in Fig. 3.

In the reaction scheme, the lignosulphonate is considered to contain enough catechol group to gel from

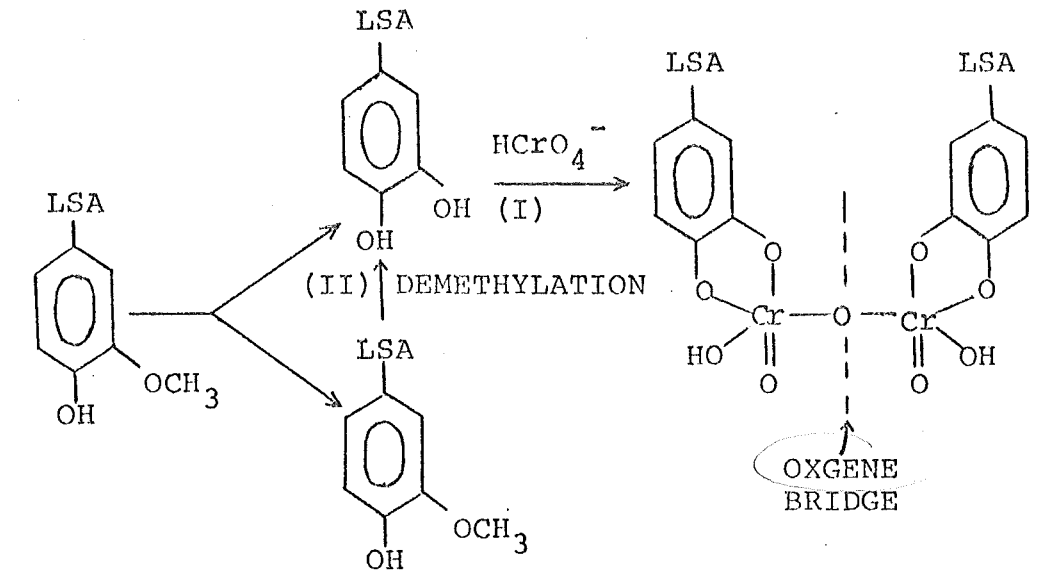


FIGURE 3: Schematic pathway for gelling reaction of ligninsulphonate with dichromate.

the beginning[19], pathway(I) while pathway (II) represents their production by demethylation in the gelling mixture. Acetic acid and heavy metal ions were found to promote both the gelling reaction and the demethylation and these reactions are different types of reaction.

Pathway(II) contributes to the gelation depending on the gelling time. If the quick intermolecular crosslinking is allowed under the reaction condition employed, the intermolecular crosslinking should predominate over the demethylation and general oxidation. If the gelling time is long, demethylation could not be neglected and would contribute to the gelation.

Since the optimum pH for the gelation reaction was 3.5 to 4.5, the active chromium species[4] is identified as the $HCrO_4^-$ which interacts with the lignosulphonate in the complexation step.

As two pendent catechol groups are required to give a crosslink, a prerequisite of gelation is that each ligninsulphonate molecule contains two or more catechol groups,[11,12] the number of which is dependent on the size of the molecule. The success of a gelation is therefore dependent on the molecular weight of the ligninsulphonate. In support of this, it has been shown that the lignin-sulphonate gels get weaker for molecular weights below 10,000 and no gel could be produced at all with molecular weight of 2,900. This was however not found to be true in our experiment with Discon and this discrepancy spawned the development of a new gelling mechanism for gelation as mentioned below and developed in Chapter V.

The condensation - dimerisation process with production of catechol-chromate crosslinks as described in Fig. 3, was held by Hayashi to be the major reaction[21] for gelation. In view of dichromate being a strong oxidant, the possibility of other types of reaction productive to polymerisation could not be ruled out. Tanaka and Senju have suggested that it is plausible that the dichromate could cause a dehydration coupling on the ligninsulphonate between benzene nuclei Fig 4, with the dichromate acting as an oxidant.

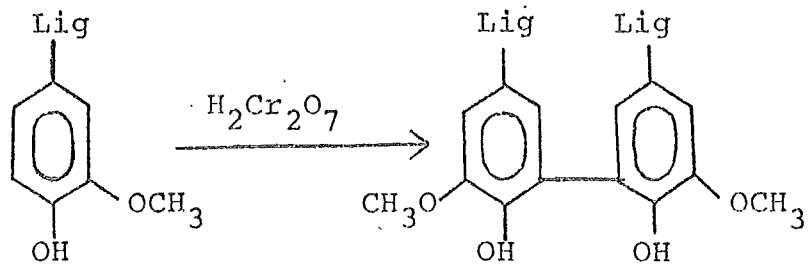


FIGURE 4: Proposed scheme for oxidative gelation of ligninsulphonate.

According to Albert,[22] dehydration coupling with dichromate proceed only on the phenolic compounds which have a tertial substituent at α-position among tetraalkyl phenols he tested. With the use of phenolic model compounds, Hayashi argued that the methoxyl group in guaiacyl compound cannot correspond to the tertial substituent group in Albert's model and so this reaction is not expected to proceed or does so extremely slowly with ligninsulphonate. Hayashi dismissed the oxidative dehydration coupling as unimportant at the early stages of gelation and at most a minor reaction.

Whatever the truth, there is no denying that calcium ligninsulphonate is a complex molecule with multiple functional groups and there is every possibility that such other reactions as chelation and salt formation may also occur and contribute to gelation. Studies on the darkening[23] of lignosulphonate with heavy metal ions yielded conclusive evidence of the existance of a second active site as yet unidentified but which is capable of stronger complexation than catechol groups.

Finally, the action of dichromate on the lignin molecule actually consisted of two different classes of reactions[4] in that there are the 'gelling' reactions and the 'oxidative-degradative' reaction. The oxidation reaction is more general and involves several types of groups on the lignin substrate which would be sensitive to attack by dichromate and leads to breakdown of molecule to smaller fragments. When conditions are such that the oxidation takes place too rapidly, (e.g. at low pH and high temperatures) the sites available for cross-linking will be destroyed and gelation will not take place.

For the gelation catalysed by the addition of heavy metal ions, very little work has been reported in the literature on the kinetics.

1.6 This Work

As has been indicated, the nature of lignin and its derivatives is variable. The lignin compound used in this work was a commercial product called Discon imported

from Scandanavia and it was therefore necessary to characterise for some of its important physical and chemical properties.

It was the initial intention when this work was begun to determine for an optimum gel mixture in terms of the various factors deemed important by the N.Z.E.D.

The conductivity of the ligninsulphonate gels for varying ligninsulphonate concentrations and metal chloride additives were examined for their properties as suitable conducting electrodes.

We have also investigated the kinetics of the polymerisation of Discon catalysed by heavy metal ions, in particular with ferric chloride which could be employed by the N.Z.E.D. in their groutings.

With respect to the above studies we investigated a number of viscometers for their suitability in the study of gelling mixtures.

A discussion on the possibilities of improving on the ideal gel mixtures for the N.Z.E.D. in the light of characterisation, conductivity, viscosity and kinetic data obtained is included in this thesis.

CHAPTER II

EXPERIMENTAL AND APPARATUS

2.1 Investigation for a Viscometer for Measurement of Viscosity of Gel.

The gelling point of a polymer mixture can be determined roughly by shaking the mixture and examining for loss of material movement. A more reliable method is the use of a penetrometer[8], but it gives only single, arbitrarily chosen point readings of the gel in its solid state and has also been shown to fail for very soft gels and gels with long setting times whose gelations are not sharp. Hayashi [4,13] in his rheological studies employed an Epprecht viscorator, a Couette type of instrument which measures for shear stress, from which the viscosity is calculated. The viscosity of gel mixtures of 11 to 15% ligninsulphonate solutions was successfully measured but it was not known whether the success of the Epprecht viscorator extends over a wider range of gel concentrations.

It was desirable for our purpose to choose a viscometer that could give a continuous measurement of the viscosity of gel mixture and be capable of working in the full range of gel concentrations from 5% to 50% ligninsulphonate mixtures.

2.2 The Rotating Spindle Viscometer

The first method investigated involved the use of a rotating viscometer in which a rotor was spun in the polymerising solution and the viscous drag on the rotor determined from the electrical power supplied to a motor. Two variations of this method were tried:

(1) A simple electric motor run from a constant voltage source through a dropping resistor in which the power consumption was monitored as a function of viscosity. The motor current was measured until stalling occured at or in vicinity of gel point.

(2) In the second variation, the motor is run at constant speed with the aid of an electronic control device and the power consumption was measured until such time slipping occured in the gel.

2.3 Theory of Motor Systems

If V is the applied voltage across the motor, power of motor in absence of external work is given by

$I_o V$ = friction losses

= mechanical and electrical (internal resistance)

$= I_o^2 R_m + I_o^2 R_i$; R_m is motor resistance

R_i is internal resistance.

Similarly, power of motor under load is

IV = friction losses + losses due to viscous drag

$= I_o^2 R_m + I^2 R_i + K\eta s$; η = viscosity

s = speed of motor

$$\therefore (I - I_o)V = K\eta s + (I^2 - I_o^2)R_i$$

Assuming R_i is small

$$(I - I_o)V = K\eta s$$

For a permanent magnet D.C. motor,

$$V \propto s$$

or $V = ks$

(a) At constant applied voltage

$$(I - I_o)V \; K\eta \; \frac{V}{k}$$

or $$(I - I_o) = \frac{K}{k}\eta$$

(b) At constant speed

$$(I - I_o)ks = K\eta s$$

$$(I - I_o) = \frac{K}{k}\eta$$

Thus for both constant voltage and constant speed systems, the current is linearly proportional to viscosity, fig. 5.

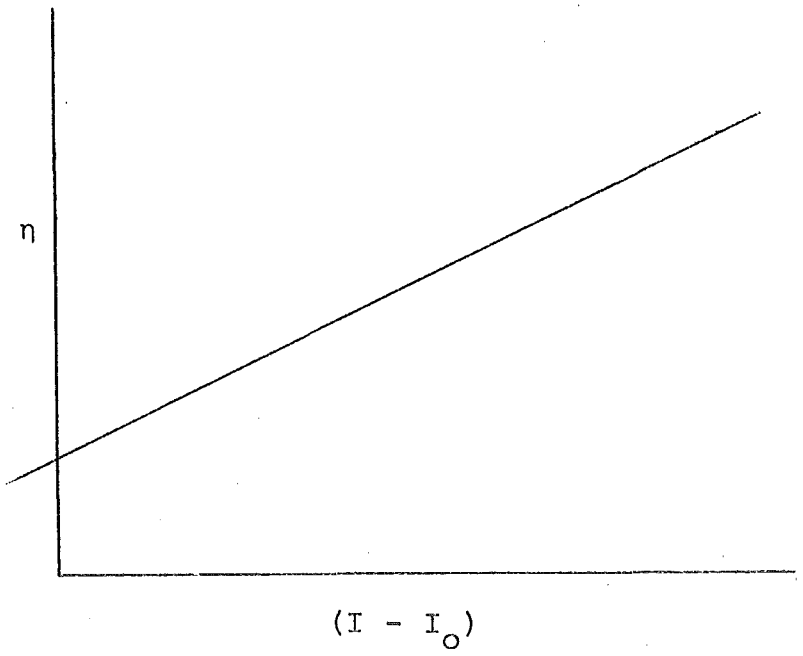


FIGURE 5: Viscosity as a function of current drawn from a D.C. motor.

During gelation, the viscosity of the polymer mixture rises steeply towards infinity with the result that the current drawn by motor would be steeply rising until the motor either stalls at constant applied voltage or slips at constant speed. The gel point could be conveniently defined as the time at which the motor stalls or slips, fig. 6.

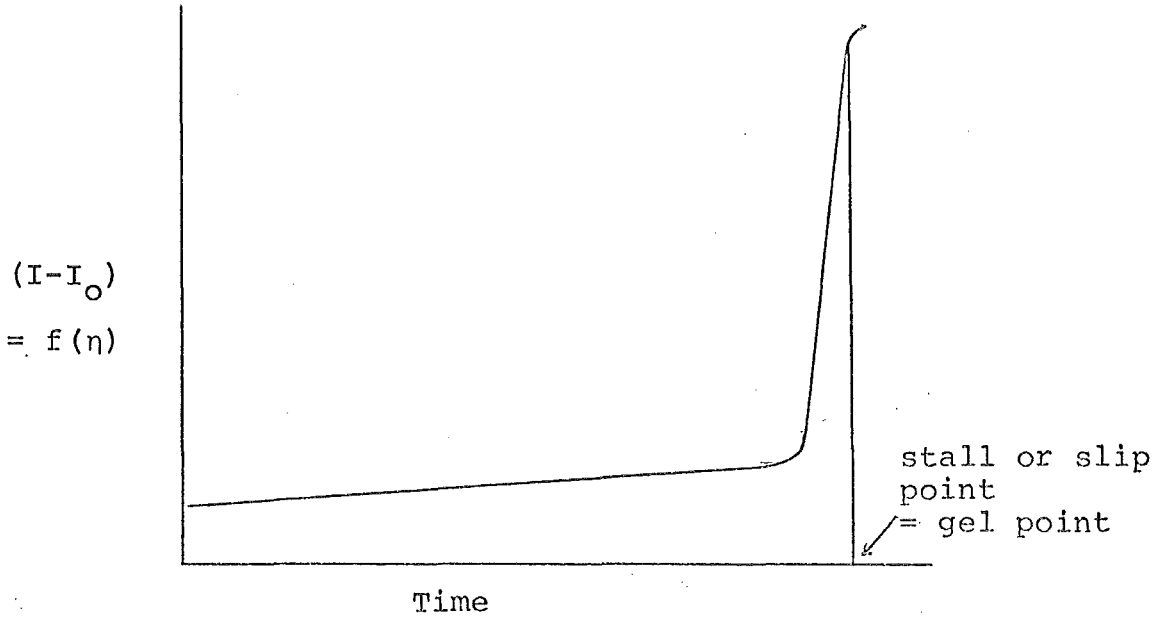


FIGURE 6: Current of motor as a function of time for a polymerising mixture.

Although the first system is not actually a constant voltage system, the current drawn would be roughly proportional to the viscosity of the polymerising gel. Due to the simplicity of the circuit, the current I and not $(I - I_o)$ would be read off an ammeter. Since the internal resistance of motor, R_i, is dependent on the motor used and increases with wear, the stall time obtained would only be reproducible for a given motor and provided that the motor does not deteriorate with use. The first motor system was found to be capable of greater sensitivity but the second system has the advantage that the current measured as $(I-I_o)$ is independent of the nature of the motor used and reproducability of readings is not suffered.

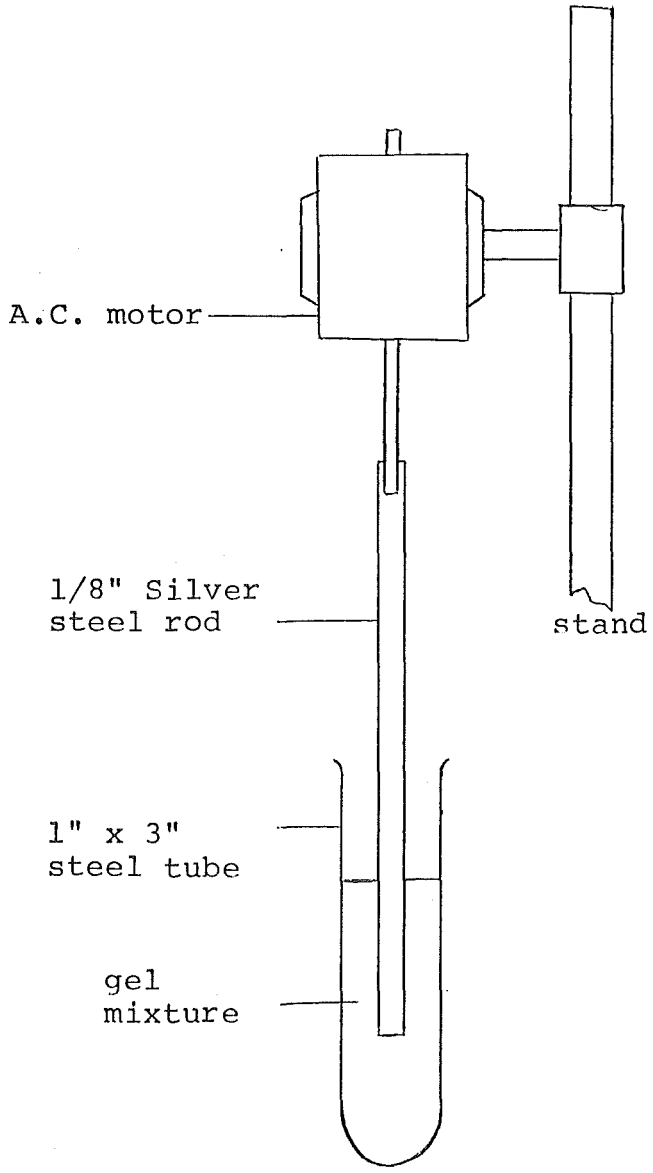


FIGURE 7: The rotating spindle viscometer.

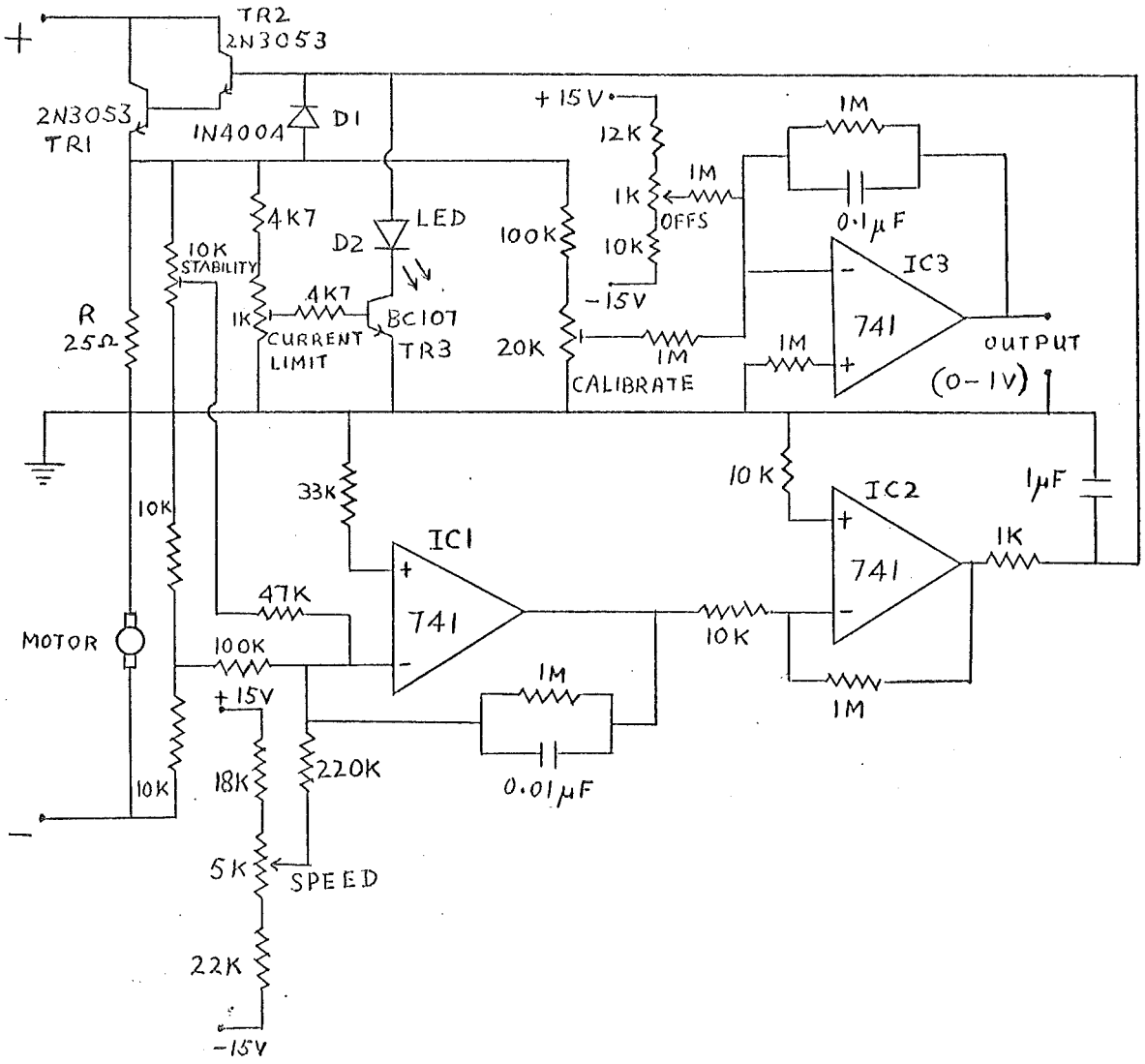


FIGURE 8: Electrical circuit for constant speed motor system.

The motor was run at constant speed by means of an electronic control the principle of the controller was that it maintained the back e.m.f. of the motor and hence its speed at a constant predetermined level with an electronic servo control.

2.4 Testing of Rotating Spindle Viscometer

The performance of the viscometer fig. 7 was examined using a mixture of 10 mls of 50% calcium ligninsulphonate plus 2.2 mls of "50%" dichromate (refer Chapter IV) solution and a typical viscosity graph obtained with the first system is given in Fig. 9.

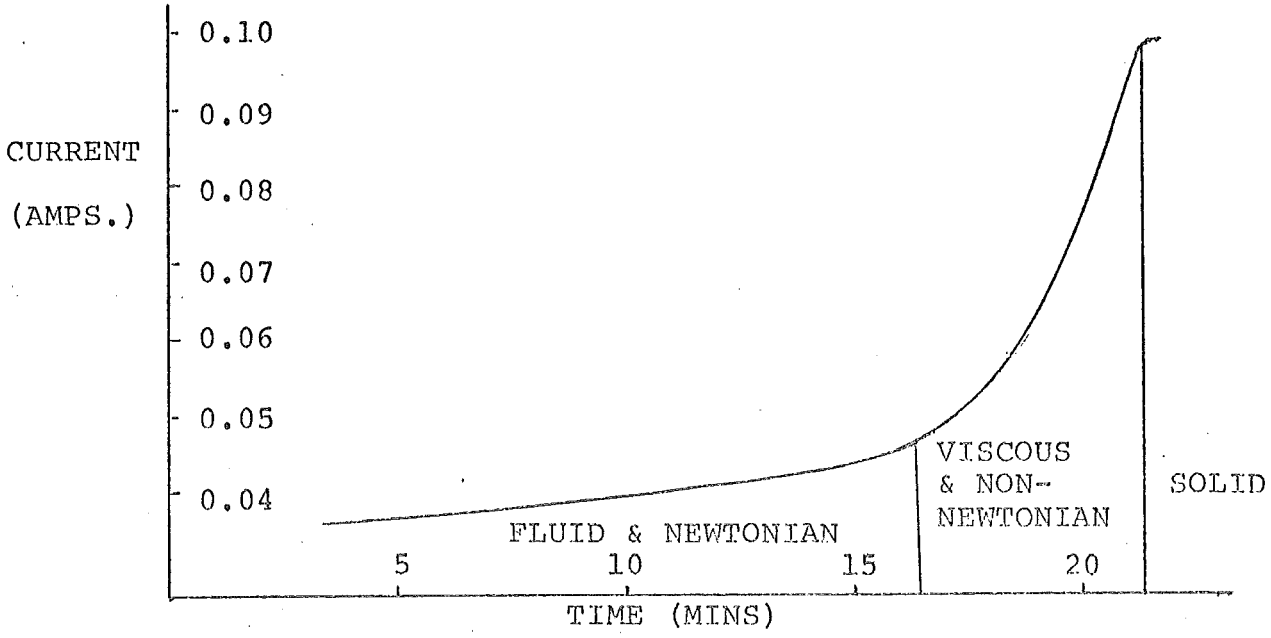
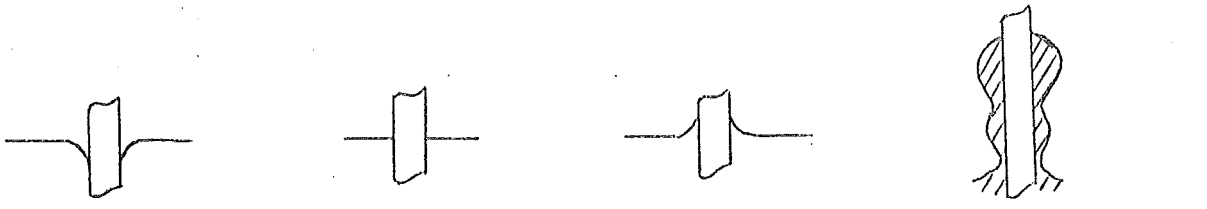


FIGURE 9: Typical rheogram for a gel mixture of 50% lignin-sulphonate using a rotating spindle viscometer (first system).



(i) Vortex created around rotor, Newtonian state.

(ii) Mixture losses vortex, point of transition.

(iii) Gel mixture starts to climb up rotor, non-Newtonian state.

(iv) Gel continue to "climb" until motor stalls.

FIGURE 10: Behaviour of meniscus of gel mixture of 50% ligninsulphonate at rotor of motor.

Characteristically the viscosity curve is horizontal or gently rising at first and then rises steeply whence the motor stalled and the gelation point is taken. Such a viscosity profile as a function of current drawn would enable an experimental gelation point to be satisfactorily determined as defined previously. Repeated runs on the same mixture showed that the gel point determined in this manner could be obtained to within 10% accuracy.

The viscosity curve appeared to be composed of three segments as was reported by Hayashi.[4,9] At the same time, the gel was observed to undergo a sequential change in physical character with time in correlation with the profile of the viscosity curve. From 0-17 minutes, the curve was quite flat and this corresponded to a fluid state of Newtonian[24] character during which the rotation of the motor created a vortex on the surface Fig. 10(i). From 17-22 minutes, the curve was steeply rising and this corresponded to an increasingly viscous state of Non-Newtonian behaviour. At the transition of Newtonian to Non-Newtonian state, the vortex 'levels' up, Fig 10(ii), then the gel gradually climbs up the rotor until at about 22 minutes, sufficient amount of gel was 'scooped' up to cause stalling of motor, Fig 10(iii) and (iv). The stage after gelation corresponds to a solid state of the polymer.

Some thought was given to the possibility that the characteristic point at which the vortex created by the rotor was lost could serve as a useful indication for

the gelling time itself. Unfortunately it was found to be sufficiently sharp only for 50% ligninsulphonate gel mixtures whereas for lower gel concentrations it extended over a period of time and could not be clearly detected.

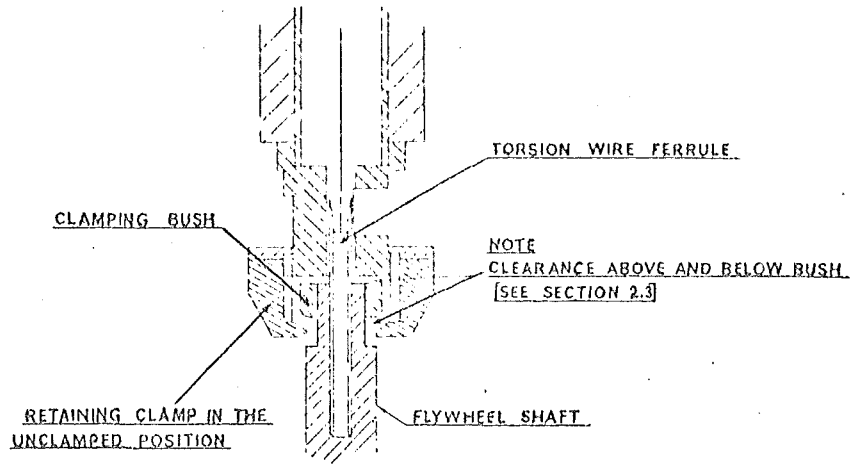
Similar observations were obtained with the constant speed system.

The success of the rotating spindle viscometers was extremely limited. It worked very well for 50% ligninsulphonate gel mixtures but failed completely for lower concentrations. The reason is that the ligninsulphonate gel is susceptible to shear and a less concentrated polymerising mixture is easily broken up by the force of the rotor which prevented gripping of the gel on the rotor to any extent resulting in a horizontal viscosity graph being recorded. In addition, such viscometers are basically not suitable for extremely low concentration gels e.g. 5% ligninsulphonate solutions, because the continuous agitation of the rotor was sufficient to prevent the formation of the gel altogether.

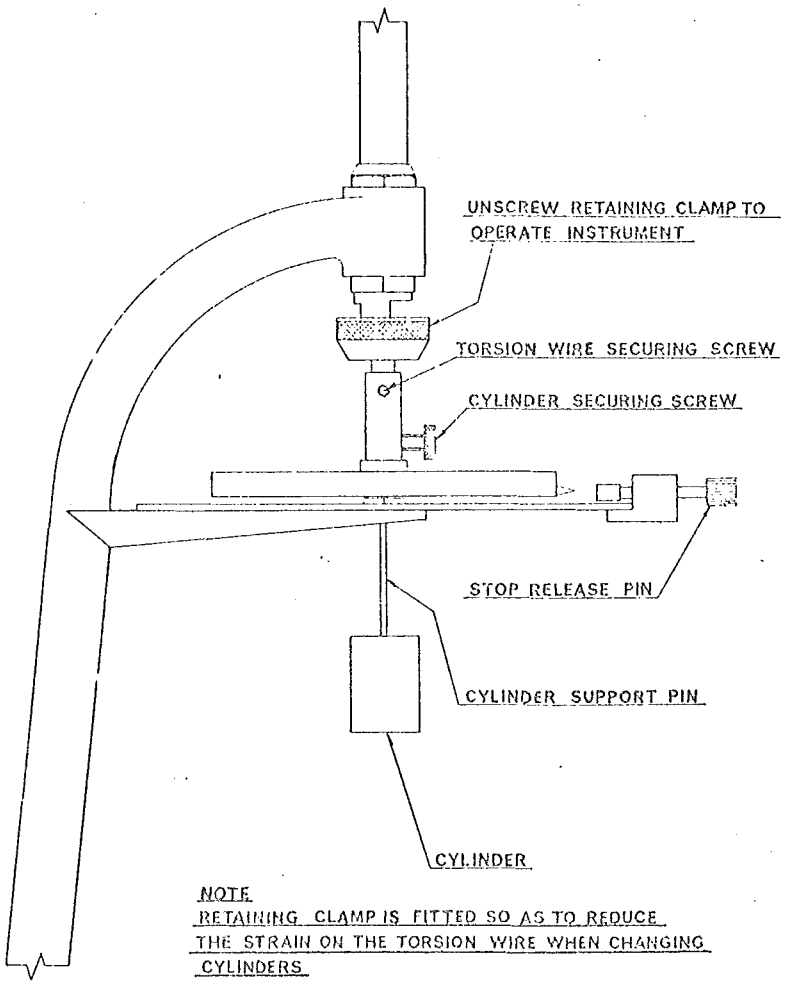
Clearly the criteria required for viscometer to work for all ranges of concentrations is that it does not involve continuous stirring movements and that it does not exert a large mechanical force on the gel. Such a viscometer was finally found in the Gallenhamp Torsion wire Viscometer.

2.5 The Gallenhamp Universal Torsion Viscometer VS-010.

Principle of use: The Torsion viscometer fig. 11 enables viscosity to be determined as a function of the angle of overswing of the flywheel which occurs when the torsion wire was wound



SECTION THROUGH RETAINING CLAMP



NOTE
RETAINING CLAMP IS FITTED SO AS TO REDUCE THE STRAIN ON THE TORSION WIRE WHEN CHANGING CYLINDERS

ASSEMBLY DIAGRAM

Drg No. R3334/69

VS-010 : VS-020 TORSION VISCOMETER

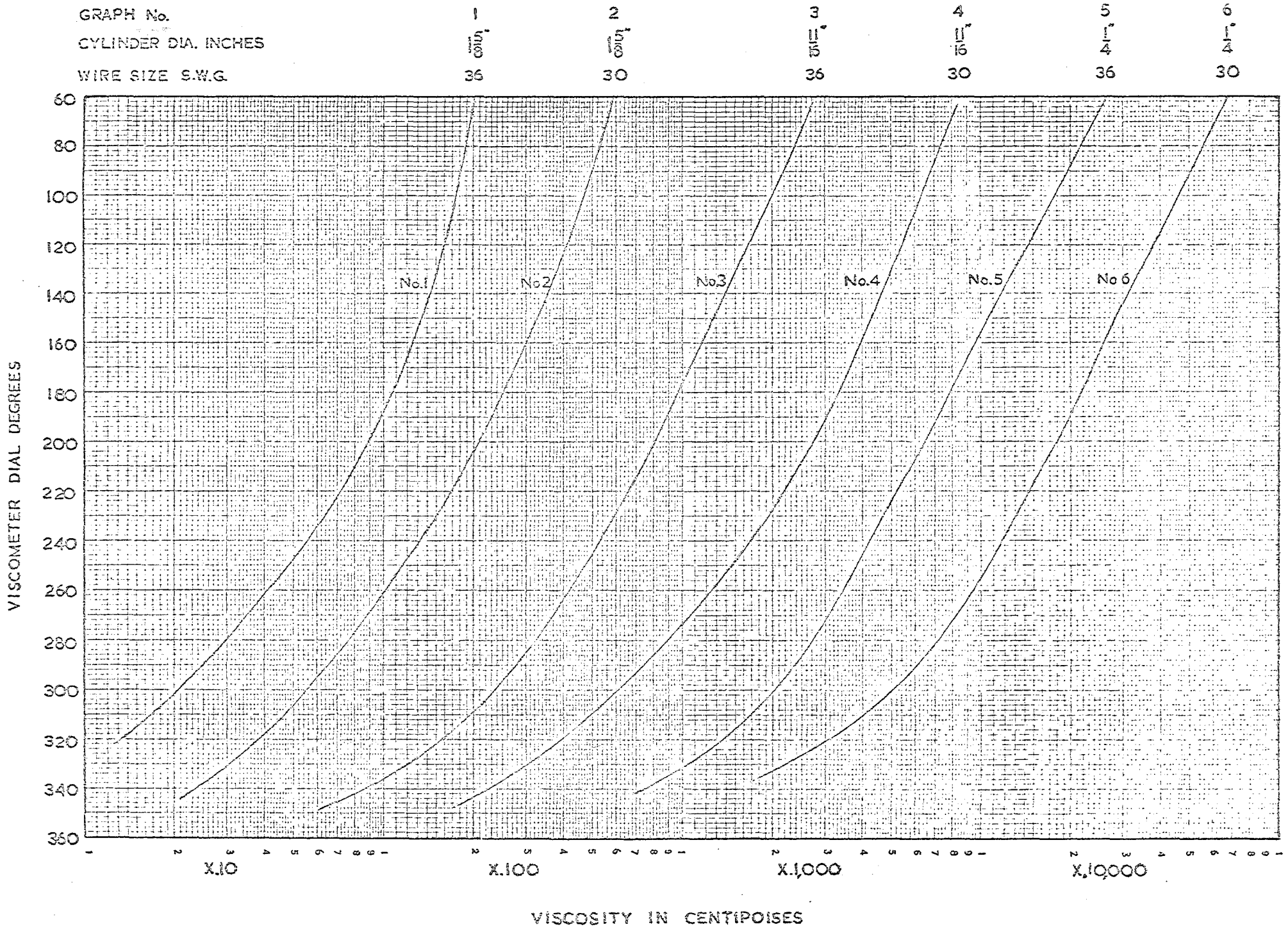

GRAPH No. 1 2 3 4 5 6
CYLINDER DIA. INCHES 15/8" 15/8" 1 5/8" 1" 1/4" 1/4"
WIRE SIZE S.W.G. 36 30 36 30 36 30
VISCOMETER DIAL DEGREES
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
No.1
No.2
No.3
No.4
No.5
No.6
X.10
X.100
X.1,000
X.10,000
VISCOSITY IN CENTIPOISES

Figure 12.

one complete turn and released. The relationship between overswing and viscosity is as defined in calibration graph fig. 12. For greatest accuracy, the torsion wire and cylinder should be chosen so that the angle of overswing should be between about 100^{o} and 300^{o}.

2.6 Method of Use and Experimental Procedure

A $1\frac{5"}{8}$ diameter cylinder and a torsion wire of S.W.G. = 36 was chosen for which satisfactory gelation points could be obtained for all concentrations of gel mixtures. The setting up and operational procedure was carried out according to the instruction manual and to extend the useful limits of the viscometer on the lignin-sulphonate gels the flywheel was wound only one half turn.

The gel mixtures for viscosity measurements were prepared as follows. Stocks solutions of ligninsulphonate and dichromate were stood in a water bath at $25^{o}C$. 30 mls of ligninsulphonate were measured out with a syringe into a beaker of 5.5 cm diameter and 5.5 cm height (call it gel-cup). Similarly 6.6 mls of dichromate were measured into a 100 ml beaker. This gave a total volume of 36.6 mls for the mixture in order that the viscometer cylinder could be completely immersed in it. For catalysed mixtures, the appropriate quantities of catalyst was weighed and dissolved in the dichromate solution. The two solutions were mixed rapidly by pouring back and forth before loading into the viscometer. For gels of less than 10% ligninsulphonate concentration, the overswing

was taken once every half minute. For long gelling mixtures of greater than 10% concentrations readings were taken once every few minutes and more frequently towards their gelation points while for quick gelling mixtures, readings were taken every half or quarter minute.

2.7 Performance of Torsion Wire Viscometer

The viscometer successfully measured for viscosity del for all gel concentrations right down to 5% by weight of ligninsulphonate solutions catalysed by ferric chloride. Basically two different sorts of viscosity-time behaviour were obtained over the range of ligninsulphonate concentration investigated i.e. 50% - 5%. Typically rheograms for mixtures of less than 10% ligninsulphonate solution and for mixtures of greater than 10% ligninsulphonate solution are given in fig . 13.

It was observed that for $\leqslant$ 10% gel mixtures, the gelation invariably exhibited only two physical stages. Initially, the viscosity of mixture stayed unchanged which corresponded to a horizontal curve and then at point of gelation, the three dimensional gel formed quite suddenly and the graph rose almost vertically. The rotation of the cylinder easily sheared the gel and the steep rise in viscosity breaks off at this point and slipping at random after.

For >> 10% gel mixtures, the gelation process always revealed three physical stages of fluid and

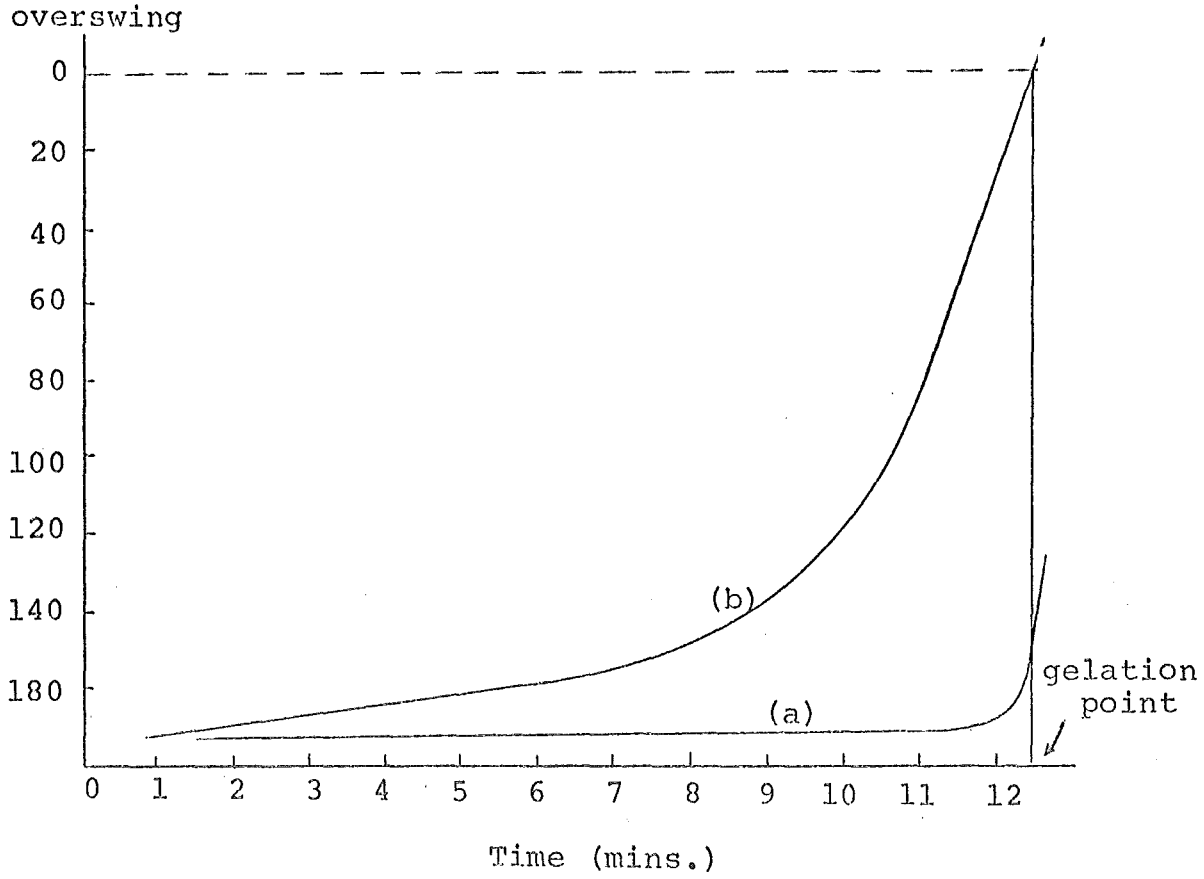


FIGURE 13: Typical rheograms of ⩽ 10% and > 10% ligninsulphonate gel mixtures of similar setting times.

Curve (a): 10% ligninsulphonate + "10%" dichromate + 10 gms ferric chloride per 100 ml mixture.

Curve (b): 50% ligninsulphonate + "50%" dichromate + 2 gms ferric chloride per 100 ml mixture.

Newtonian state, viscous and non-Newtonian state and the solid gel state upon gelation (refer rotating spindle viscometer). The viscosity commenced to rise during the viscous state and continued past the zero overswing mark as the mixture turned solid, but the steeply rising portion of curve was never as dramatic as $\leqslant$ 10% gels and was usually spread over a few minutes. The extent of the viscous state was variable and was roughly proportional to the gelation time of the mixture. For quick setting gels e.g. 50% lignin-sulphonate plus "50%" dichromate plus 10 gms ferric chloride per 100 mls mixture, all three stages merged together.

The gelation point for gels of $\leqslant$ 10% ligninsulphonate solutions could be appropriately defined as that time corresponding to the sharp rise in viscosity. Since the rise was so steep there was little need to define for an exact point on the rise to be taken and an arbitrary spot in that region was sufficient; the full rise of the curve was never available anyway due to shearing of the gel. No such convenient gelation point for >> 10% mixtures could be selected from their rheograms and their gelation points were arbitrarily defined as that time corresponding to zero overswing of the flywheel of viscometer. This definition was not totally without justification. At this point the gel was in a very viscous plastic state and if this was gel at its infant state then it should not dissolve or disintegrate in water. Various gel mixtures were tested for dissolution in water at zero

overswing and this was found to be true whereas mixtures prior to this dissolved promptly. The gelling point at zero overswing could be considered to be close to the chemical gelation point.

The success of the viscometer for all concentrations of the gel mixtures rested on two simple reasons. The force of rotation of the cylinder generated from the torsion in the wire was small and this worked to lower the concentration limit of gel mixtures capable of surviving the shear by a lightly rotating cylinder down to below 5% ligninsulphonate mixtures. Contrast this with the lower limit of 40% ligninsulphonate mixtures for the rotating spindle viscometer. Secondly, the fact that the viscometer was not a continuous stirring system was critically important and enabled those $\leqslant$ 10% gel mixtures whose gelations were particularly sensitive to mechanical shear to form in a minimal of disturbance. The viscosity readings being taken at intervals minimised the shearing effects of the cylinder on the gel mixture.

The shear effects of the cylinder was further reduced in the setting of the torsion head and selection of the torsion wire and cylinder. In fixing these three factors, an optimisation between reduced shear, decreased period of swing versus decreased sensitivity of instrument was sought for each. To this end the torsion head was set such that the flywheel would be wound only one half turn and using a large cylinder and wire size.

The only inadequacy of the instrument was the problem of temperature control. The torsion viscometer was provided with a cup lined with a jacket through which water could be circulated for control of temperature. For a gelation mixture this was found to be difficult, not so much as to the shortcomings of the viscometer but the nature of the polymerising reaction itself. Generally the rate of heat evolved was proportional to the setting time and to the concentration of ligninsulphonate and ferric chloride added. Thus for quick gelling mixtures of less than 30 minutes and for mixtures of [lignin-sulphonate] $\geqslant$ 20% and [ferric chloride] $\geqslant$ 6 gm/100 ml mixture, the amount of heat evolved was large enough to be felt by touch and for a 50% ligninsulphonate mixture with ferric chloride of concentration of 10 gm/100 ml mixture, the heat evolved was intense enough to raise the temperature above 35^{o}C. When such large amounts of heat are produced in a short time by these gels, it was impossible for any cooling system to dissipate the heat rapidly enough. Hayashi[4] reported that the gelation was not largely affected by temperature variation. This was found to be approximately true for quick setting gels while slow gelling mixtures were sensitive to room temperature change (refer Chapter V) and would benefit most from the use of a water jacket. As most catalysed gel mixtures of all concentrations were not long gelling, it was decided that the water jacket would be dispensed with and a plain gel-cup was used which allowed for speed

of viscosity measurements. Nonetheless, the initial temperature of the stock solutions was controlled by thermostating the room.

2.8 Measurement of Cell Resistance and Capacitance of a Ligninsulphonate Gelling Mixture

The resistive and capacitive components of gel impedence between the electrodes of a probe in the polymerising electrolyte was determined using an A.C. transformer ratio arm inductance bridge at 1 K.Hz. frequency. The probe used consisted of a pair of platinum electrodes and carrying a cork collar. The probe, Fig 14 was made with the ends of the platinum tips well embedded into the glass at ~ 1 cm apart.

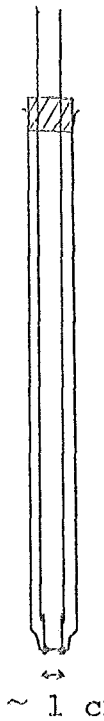


FIGURE 14: The platinum electrode probe.

2.9 Experimental Procedure and Special Experimental Consideration

The cell mixtures were made by measuring out 10 mls of ligninsulphonate stock solution into a 1" x 3" test tube and 2.2 mls dichromate solution into another containing appropriate amounts of ferric chloride. The two portions were mixed thoroughly, the electrode dipped into the mixture and inserted in place with the cork collar. The cell was placed in a thermostated bath at 25°C and the gel resistance determined as a function of time.

The condition of the electrode was found to be critical in giving reproducable rates of change of resistance. Glass strongly absorbs dichromate ions and those absorbed between the platinum tips of electrode would significantly increase the local concentration of dichromate ions which would 'promote' the adjacent portion of gel mixture. The dichromate ions were removed by the following cleansing procedure: the electrode was scrubbed with a stiff brush and dipped into a 0.8 gm potassium permanganate in 200 mls concentrated sulphuric acid solution. The solution was heated to 100°C and then left to stand for 30 minutes. The electrode is then placed under running distilled water for at least 30 minutes and dried with tissue paper.

CHAPTER III

CHARACTERISATION OF REAGENTS USED

3.1 Introduction

Discon is manufactured by the action of calcium bisulphate on the lignin of Scandanavian softwood. It is a complex compound and its exact composition is uncertain. The main constituents are stated by the manufacture to be:

Calcium lignosulphonate	60% by weight
Calcium salts of lower molecular weight, organic acids	10% by weight
Reducing sugars (mainly hexoses)	26% by weight
Other constituents	4 % by weight
	100%

Other average data:

Moisture content	5% by weight
Lime as CaO	1% by weight
pH of aqueous solution 1% conc.	4.6% by weight
Bulk density	0.5 kg/ℓ or 50 kg/m^3.

3.2 Determination of heavy metal ion impurities in technical ligninsulphonate (Discon) and sodium dichromate

Besides containing above impurities mentioned, commercial ligninsulphonate always has an occasion to react with heavy

metallic ions contained in wood components during the pulping and isolation processes and forming heavy metallic ligninsulphonate complexes. The heavy metal ions have been shown to promote the gelling reaction of ligninsulphonate by Akakane[8] and depending on their concentrations present could contribute to the gelling times, the extent of their participation is of interest in our kinetic studies on the catalysed gelation later on. It is therefore useful to evaluate for the amount of these ions present in technical ligninsulphonate; these would include those transition metals thought to be catalytically active as electron transfer agents e.g. Fe(III), Cu(II) and Mn(II) - refer Chapter V. The concentrations by weight of these impurities in Discon measured by atomic absorption spectroscopy were found to be Iron (41.4 ppm), Copper (0.9 ppm) and Manganese (106.1 ppm).

The sodium dichromate reagent is also of commercial grade in an unrefined form and was used throughout our experiments for optimum gel mixtures and kinetic studies. For similar reasons the amount of heavy metal ions present was also determined, they were Iron (19.7 ppm), Copper (4.4 ppm) and Manganese (2.7 ppm).

3.3 Determination of molecular weight of calcium ligninsulphonate (Discon)

The molecular weights of soluble lignin derivatives have been found to cover a wide range and depending on the

source of wood, method of isolation and method of molecular weight determination, ranged from as low as 324[11] to values greater than 10^6, which is characteristic of non-linear polymers.

Such a wide polydispersity of lignin always lead to a certain degree of indeterminancy in ascribing a value of molecular weight to a given sample of the polymer. This problem is further compounded by the fact that any purification process adopted will always influence the size of particles being purified[6].

Though the degree of polydispersity Mw/Mn, (where, Mw = weight average molecular weight and Mn = number average molecular weight) is accepted by some to be a more independent and truer quantity,[11] the average molecular weight obtained and defined in terms of a particular method of purification and measurement of the molecular weight could still remain a useful characterisation.

The molecular weight of Discon was determined by first converting to ligninsulphonic acid by action of concentrated sulphuric acid on an aqueous solution of Discon at 100°C. The solid impurities and calcium sulphate precipitate formed were filtered and the ligninsulphonic acid precipitated by slowly mixing with vigorous stirring in ethanol. The white flocculent precipitate was centrifuged, collected and repurified with ethanol. The purified acid was dried under reduced pressure with a mercury distillation line for five hours and its molecular weight was determined with a Mechrolab

Vapour Pressure Osmometer Model 301A using purified methanol as solvent and azobenzene as calibration sample. A purified sample of calcium ligninsulphonate was also obtained by dissolving a filtered aqueous solution of Discon in ethanol and precipitated by addition of ether. The precipitate was repurified a second time and dried in a vacuum line and the percentage of calcium content was determined spectrometrically. From these data, the molecular weight of calcium ligninsulphonate from Discon was obtained as 654.0.

Compared to average weights reported by other researchers[11] the value of 654.0 lies at the lower end of the normal range of molecular weights of the ligninsulphonate. Probably this was only the smaller faction of ligninsulphonate retained by the purification method employed and also the fact that the number average molecular weights are biased towards low values by small molecular weight constituents.

According to Hayashi's mechanism, gelation with such a sample would not be possible as it would not have the minimum of two catechol groups to permit continuous crosslinking.[12] Surprisingly, a sample of purified Discon or the acid had in fact gelled thus raising doubts as to the adequacy of Hayashi's mechanism and the measure of the number of catechol groups as an appropriate index for occurance of gelation.

3.4 Determination of "Equivalent Weight Unit of Molecule"

The calcium ligninsulphonate molecule may be pictured as a long chain molecule with sulphonate groups attached at intervals along the polymer so that the section of the molecule between two sulphonate groups could be taken as an average repeating unit for purposes of analysis. We shall define the equivalent weight unit of calcium ligninsulphonate as that weight of molecule between two adjacent sulphonic acid groups. This concept would enable us to evaluate for the number of monomeric molecules between sulphonate groups.

An expression for equivalent weight unit of ligninsulphonate could be derived as follows:

Suppose 1 gm of ligninsulphonate contains y gms of Ca^{2+} or $\frac{y}{40.08}$ moles of Ca^{2+}.

$\therefore$ 1 gm of ligninsulphonate contains $\frac{y}{40.08}$ moles of $R(SO_3^-)_2$ which would weigh (1-y) gms.

$\therefore$ Weight of $R(SO_3^-)_2$ per mole of $Ca^{2+} = \frac{(1 - y)}{(y/40.08)}$

i.e. Equivalent weight unit, $R(SO_3^-)_2 = \frac{(1-y)40.08}{y}$

The calcium content of a known concentration of purified calcium ligninsulphonate was determined with the atomic absorption spectrometer. From this the equivalent

weight unit was calculated to be 660.0. It is approximately equal to its average weight within experimental limits indicating that on the average, a ligninsulphonate molecule contains two sulphonate groups. And assuming Discon is of coniferous softwood, each equivalent weight unit would contain 3.5 monomeric units (molecular weight = 184)[3].

3.5 Determination of stoichiometry of reaction of calcium ligninsulphonate with dichromate

The stoichiometric ratio between ligninsulphonate and dichromate was determined by titration of an excess of dichromate after completion of gelation with a ferrous solution. The end-point in the direction of Iron (II) is not satisfactory and back titration was employed by adding a known excess of ferrous compound which was then titrated with a standard potassium dichromate solution. The polymerised gel was made from an uncatalysed mixture of 10 mls of 50% ligninsulphonate plus 2.2 mls of "50%" dichromate and allowed to set for twenty-four hours. The gel was minced with a "Waring" blender for at least 10 minutes and washed into a litre flask. A 25 ml portion was filtered and the filtrate was titrated with ferrous ions in the manner described above.

654 gms (one molecular weight) of calcium ligninsulphonate was found to react with ~ 0.5 moles of dichromate for gelation and if the excess of dichromate present does not

serve any useful role in the gelation process, the amount of dichromate employed in the composition of "1:1" gel mixtures in Chapter IV could be reduced by 43%.

Mechanistically, the stoichiometric result is particularly significant. On the basis of Hayashi's mechanism illustrated in figs 2 and 3, there would be just sufficient dichromate to form the chromate-esters during stage one if all the added dichromate were involved. However not all was used and the stoichiometric ratio indicates that only about half of the dichromate was actually converted. It is evident that the amount of dichromate consumed and held in the crosslinks in a sample of Discon could not be sufficient to facilitate the formation of the catehol-chromate bridges. The results can only be interpreted in terms of an oxidative polymerisation (Chapter I) for if each site of oxidation requires the transfer of one electron, the reduction of one dichromate would bring about six sites of cross-linking for every pair of ligninsulphonate moleculesor three cross links per polymer molecule.

3.6 Spectrometric characterisation of calcium ligninsulphonate

(a) Ultraviolet absorption of ligninsulphonate

Ultraviolet spectra of different lignin preparations are usually quite similar[11]. The typical spectrum, fig.15(a), decreases from a maximum near 205 mμ to a shallow minimum near 260 nm. with a pronounced shoulder near 230 nm. The minimum is followed by a characteristic lower maximum near

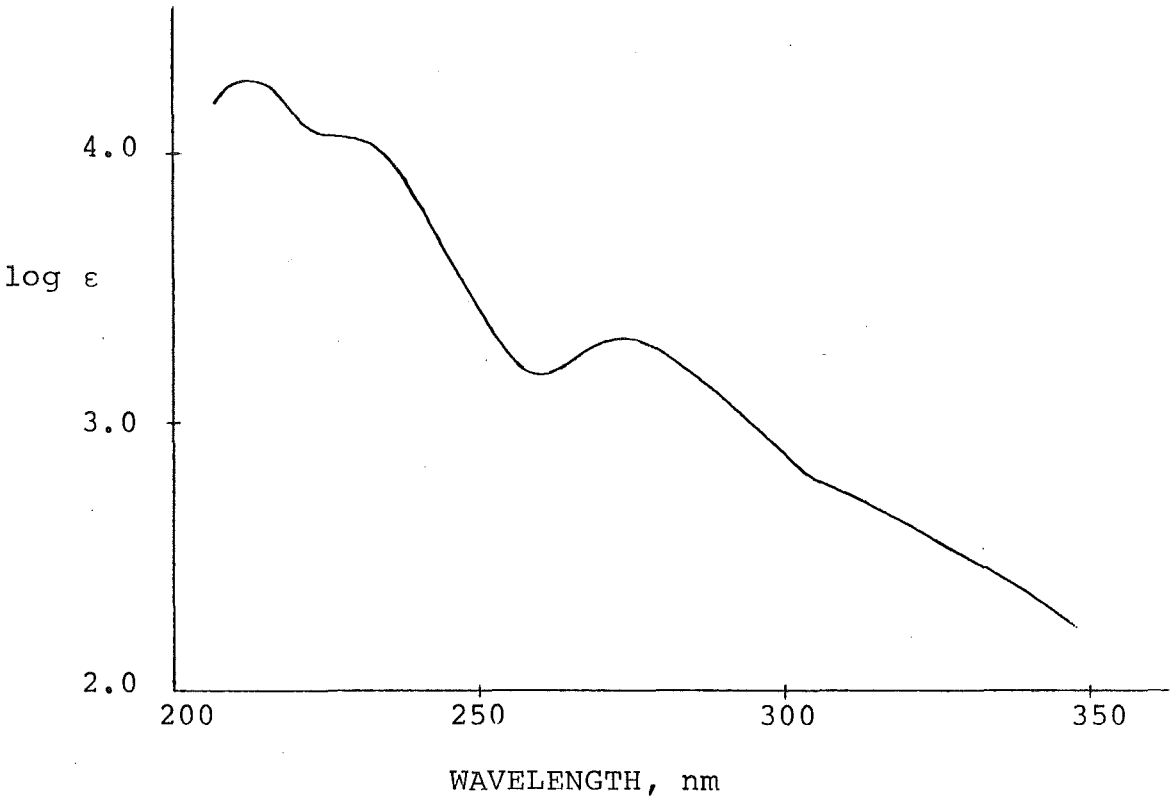


FIGURE 15(a): Ultraviolet absorption of ligninsulphonic acid.

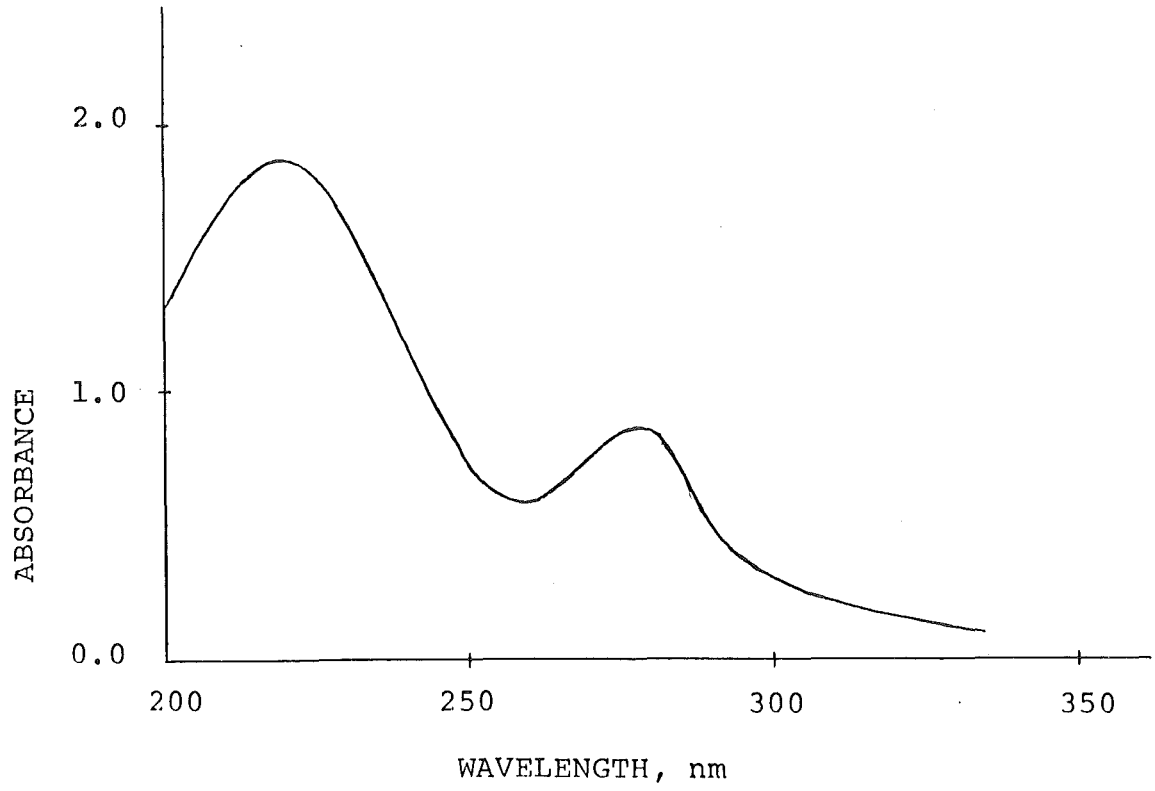


FIGURE 15(b): Ultraviolet absorption of Discon (0.002%) with the Shimadzu Spectrometer.

280 nm and then a gradual decrease in absorbance towards the visible range of the spectrum. Kleinert and Joyce[6] reported that the absorption at 205 nm, unlike that at 280 nm is characteristic of the lignin. The spectrum has been resolved and found to be composed of six symmetrical absorption bands at 228, 262, 282, 312, 331 and 351 nm corresponding to different phenylpropane units that constitute the polymer.

The ultraviolet spectrum of Discon was measured with a Shimadzu Recording Spectrometer. For a 0.002% solution, two maxima at 219 and 282 nm and a minima at 262 nm were obtained, fig. 15(b). No shoulder at around 230 nm was obtained as mentioned by Goldschmid.[11]

(b) Visible spectrum of Discon

The absorption band of ligninsulphonate in the visible spectrum is mainly at the ultraviolet end which results in its characteristic brown colour. The absorbance curve of Kraft lignin[25], fig 16(a) shows the aromatic maximum at 280 nm, a shoulder around 340 nm and a steady reduction in the absorption in the visible region.

A 1% solution of Discon gave only a well formed peak at 392 nm which falls away rapidly at lower wave lengths, fig 16(b).

(c) Infrared spectrum of Discon

The infrared spectrum of lignin is a function of the method of isolation and the nature of phenylpropane units

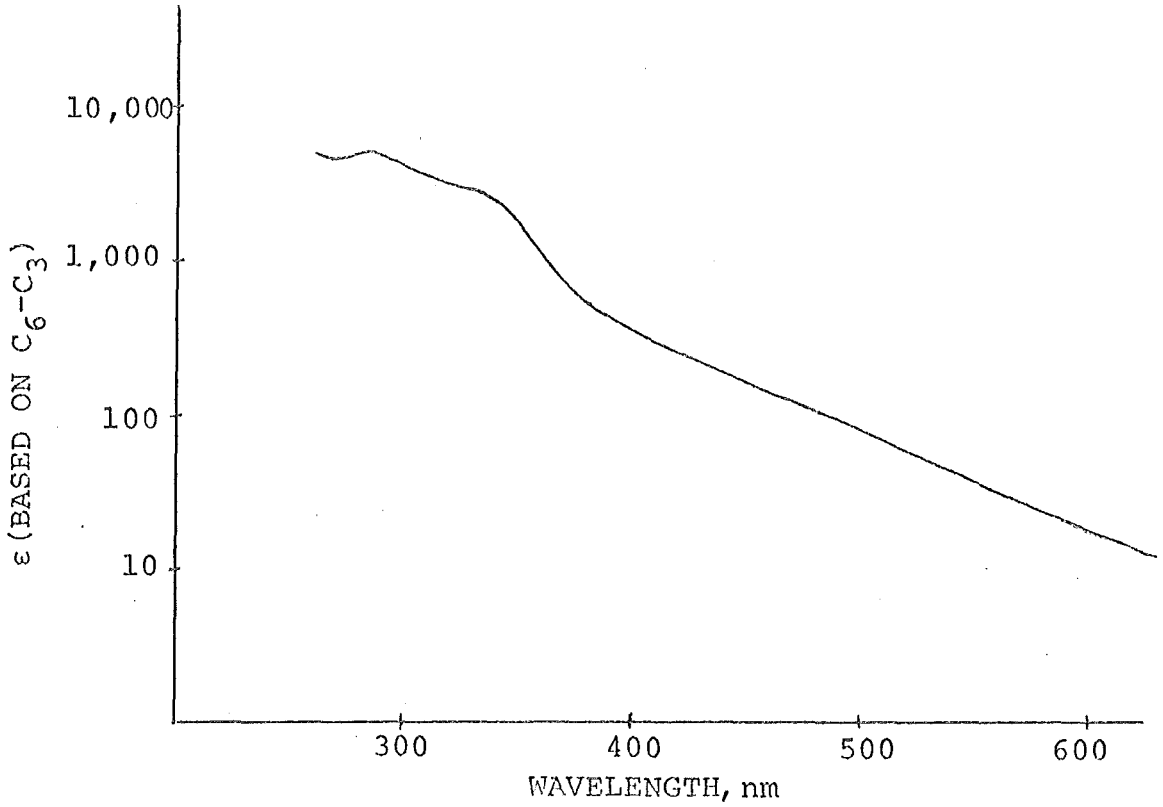


FIGURE 16(a): Visible absorption of Kraft lignin

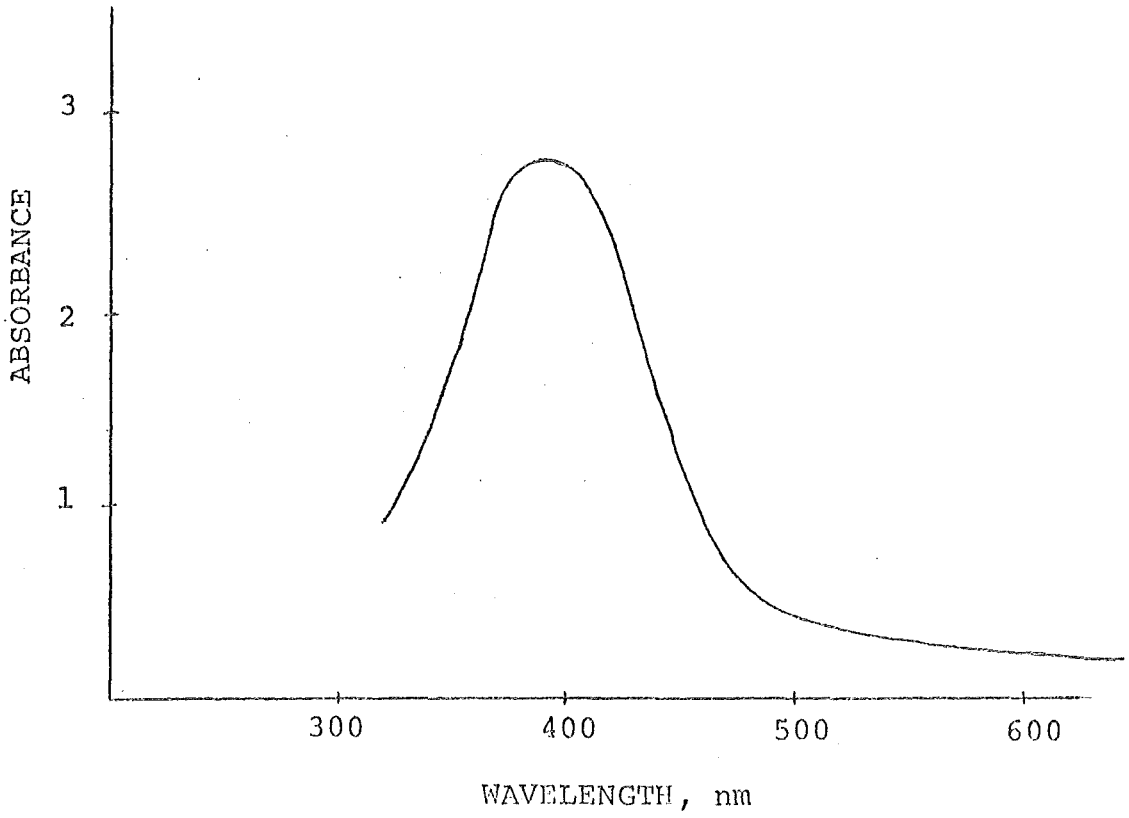


FIGURE 16(b): Visible absorption of 1% Discon

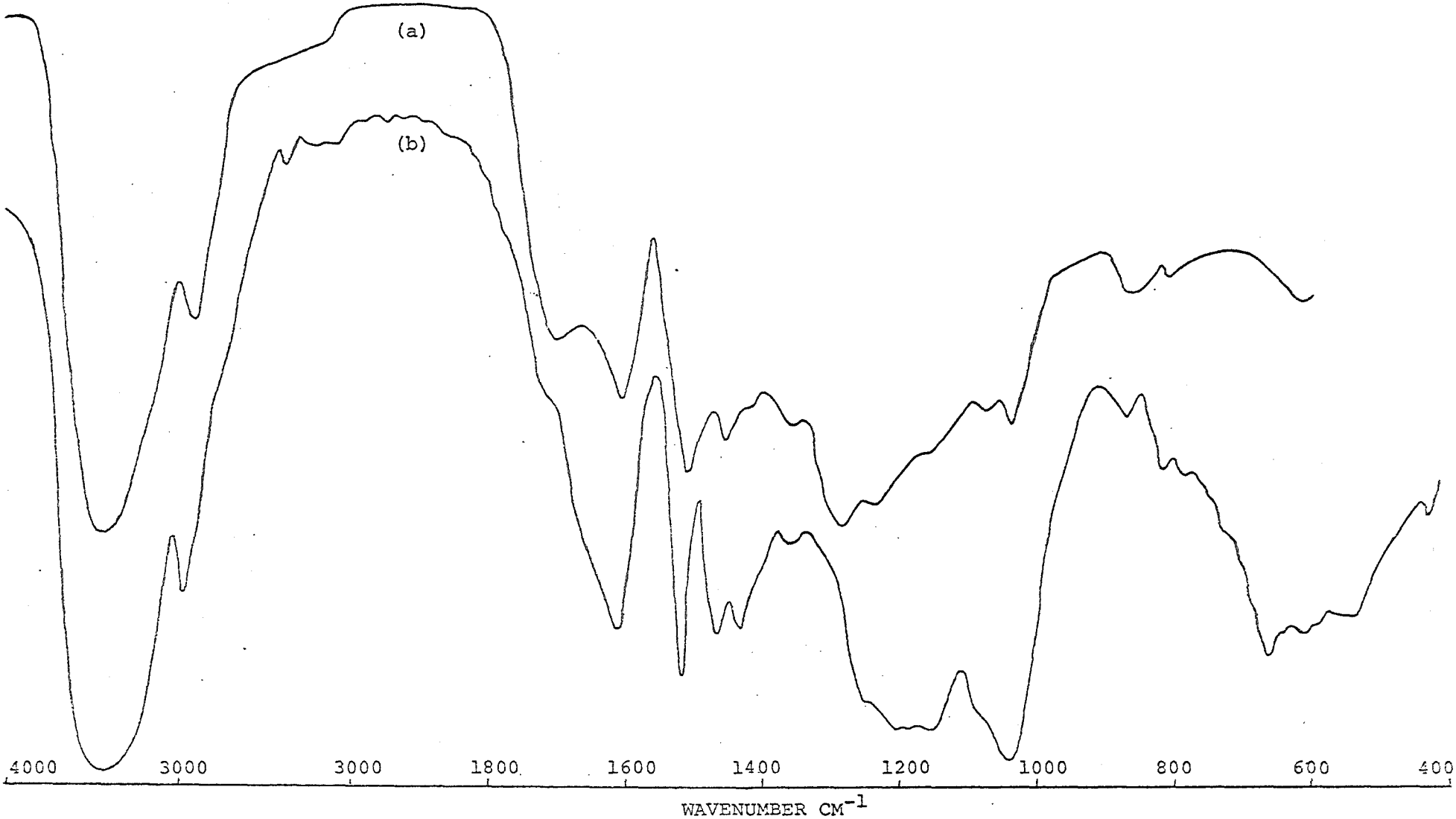


FIGURE 17: (a) KBr infrared spectrum of lignin isolated from western hemlock wood by the Kraft process.

(b) KBr infrared spectrum of Discon.

composing the polymer[...] i.e. guaiacyl or guaiacyl-syringyl lignin. The major absorption band frequencies and the most probable assignment of each band in the two types of lignin has been determined. In general with polymers, even the slightest differences in spectra e.g. relative heights of neighbouring absorption bands, the presence of weak shoulders etc. are of considerable significance. A typical spectrum from a potassium bromide wafer of lignin isolated from western hemlock wood from the Kraft process is given in fig 17.

In contrast, a similar infrared spectrum of Discon, showed considerable differences in the fine details of absorption bands.

Together with large differences also recorded in ultraviolet and visible spectrograms of Discon from those of typical samples reported in literature, it would appear that Discon is an atypical product as was also suggested by its low molecular weight of 654.0 and the ability of a purified sample to gel with little difficulty if sufficiently concentrated.

CHAPTER IV

DETERMINATION OF OPTIMUM GEL MIXTURES CATALYSED BY FERRIC CHLORIDE FOR THE N.Z.E.D.

4.1 Determination of gelling times of varying lignin-sulphonate-dichromate mixtures with varying additions of ferric chloride using the Universal Torsion Viscometer.

Preliminary studies conducted by the N.Z.E.D.[1] on the gelation of calcium ligninsulphonate by the action of dichromate suggested a setting time of about forty minutes was required to allow for completion of injection of grouting into the ground and compositions based on the following recipes have been investigated.

(1) 100 mls of 50% ligninsulphonate together with 22 mls of dichromate solution (850 gms/litre).

(2) 100 mls of 40% lignin sulphonate together with 30 mls of dichromate solution.

Mixtures containing lower concentrations of lignin-sulphonate were found to give gels of setting times longer than forty minutes in the absence of a catalyst and were not used.

Since a mixture of 100 mls of 50% ligninsulphonate solution plus 22 mls of dichromate (850 gms/litre) solution produced a satisfactory gel, we have adopted this

as our "parent" mixture from which series of variations were made by changing the ligninsulphonate concentration, the dichromate concentration as a function of ligninsulphonate: dichromate ratio and concentration of ferric chloride added.

Ligninsulphonate solutions of 50%, 40%, 30%, 20%, 10% and 5% concentrations by weight were prepared. If a solution of 850 gms/litre dichromate is defined as "50%" and a "40%" solution is made by dilution of a "50%" solution by a factor of 4/5 by weight, then "30%", "20%", "10%", "5%", "2.5%" and "1.75%" dichromate solutions were similarly made.

All gelling mixtures were composed of 30 mls of ligninsulphonate solutions to 6.6 mls of dichromate solutions to give a total of 36.6 mls. Series of gel mixtures of fixed ligninsulphonate: dichromate ratios were made as follows: 1:1 ratio mixtures were those composed of 50% plus "50%" solutions, 40% plus "40%" solutions, 30% plus "30%" solutions etc; 1:½ ratio mixtures were those composed of 50% plus "25%" solutions, 40% plus "20%" solutions, 30% plus "15%" solutions etc. Similarly for the 1:¼ and 1:2 ratio series. For each of these basic mixtures, weights of 2,4,6,8 and 10 gms of ferric chloride per 100 mls mixture were added according to procedure described in Chapter II and their setting times obtained by measuring the viscosity change with time using the torsion wire viscometer.

4.2 Results of setting times of gel mixtures catalysed by ferric chloride.

Table 1: Setting time of gel mixtures catalysed by ferric chloride determined by torsion wire viscometer.

A. 1:1 mixtures

(a) 50% ligninsulphonate + "50%" dichromate + X gms of ferric chloride/100 ml mixture.

Mixture	Gms of ferric chloride per 100 ml mixture.	Setting times (mins.)
(1)	2	12.30
(2)	3	9.00
(3)	4	6.85
(4)	6	2.23
(5)	8	0.73
(6)	10	0.26

(b) 40% ligninsulphonate + "40%" dichromate + X gms of ferric chloride/100 ml mixture.

Mixture	Gms of ferric chloride per 100 ml mixture	Setting times (mins.)
(7)	2	25.80
(8)	3	15.50
(9)	4	7.10
(10)	6	1.30
(11)	8	0.50
(12)	10	0.28

(c) 30% ligninsulphonate "30%" dichromate + X gms Ferric chloride/100 ml mixture.

Mixture	Gms of ferric chloride per 100 ml mixture	Setting times (mins.)
(13)	2	60.00
(14)	3	18.40
(15)	4	4.35
(16)	6	1.00
(17)	8	0.63
(18)	10	0.53

(d) 20% ligninsulphonate + "20%" dichromate + X gms ferric chloride/100 ml mixture.

Mixture	Gms of ferric chloride per 100 ml mixture	Setting Time (mins.)
(19)	2	80.00
(20)	3	7.50
(21)	4	2.83
(22)	6	1.50
(23)	8	1.40
(24)	10	1.68

(e) 10% ligninsulphate +"10%" dichromate + X gms ferric chloride/100 ml mix.

Mixture	Cms of ferric chloride per 100 ml mixture	Setting times (mins.)
(25)	2	20.90
(26)	3	5.35
(27)	4	3.80
(28)	6	4.40
(29)	8	7.90
(30)	10	12.40

(f) 5% ligninsulphonate "5%" dichromate + X gm ferric chloride/100 ml mix.

Mixture	Gms of ferric chloride per 100 ml mixture	Setting Times (mins.)
(31)	2	2.50
(32)	3	2.50
(33)	4	3.50
(34)	6	9.60
(35)	8	27.50
(36)	10	116.50

B. 1:½ mixtures

(a) 50% ligninsulphonate + "25%" dichromate + X gms ferric chloride/100 ml mix.

Mixture	Gms of ferric chloride per 100 ml mixture	Setting time (mins.)
(37)	2	102.00
(38)	4	20.20
(39)	6	2.65
(40)	8	0.67
(41)	10	0.34

(b) 40% ligninsulphonate + "20%" dichromate + X gms ferric chloride/100 ml mix.

Mixture	Gms of ferric chloride per 100 ml mixture	Setting time (mins.)
(42)	2	97.00
(43)	4	9.00
(44)	6	1.30
(45)	8	0.60
(46)	10	0.50

(c) 30% ligninsulphate "15% dichromate + X gms ferric chloride/100 ml mixture

Mixture	Gms of ferric chloride per 100 ml mixture	Setting times (mins.)
(47)	2	173.00
(48)	4	3.47
(49)	6	1.33
(50)	8	0.98
(51)	10	1.05

(d) 20% ligninsulphonate "10%" dichromate + X gms ferric chloride/100 ml mixture

Mixture	Gms of ferric chloride per 100 ml mixture	Setting times (mins.)
(52)	2	87.00
(53)	4	5.35
(54)	6	3.73
(55)	8	4.90
(56)	10	37.00

(e) 10% ligninsulphonate + "5%" dichromate + X gms ferric chloride/100 ml mixture

Mixture	Cms of ferric chloride per 100 ml mixture	Setting times (mins.)
(57)	2	4.60
(58)	4	2.50
(59)	6	5.60
(60)	8	-
(61)	10	-

(f) 5% ligninsulphonate + "2.5%" dichromate + X gms ferric chloride/100 ml mixture

Mixture	Cms of ferric chloride per 100 ml mixture	Setting times (mins.)
(62)	2	2.00
(63)	4	3.50
(64)	6	-
(65)	8	-
(66)	10	-

Note: - means no gelation.

C. 1:¼ mixtures

The 50% and 40% ligninsulphonate mixtures were on the verge of gelling (i.e. became very viscous and "colloidal") but did not gel, while less concentrated mixtures did not show any imminent signs of gelling at all.

D. 1:2 mixtures

(a) 50% ligninsulphonate + saturated dichromate + X gms ferric chloride/100 ml mix.

Mixture	Gms of ferric chloride per 100 ml mixture	Setting times (mins.)
(67)	2	6.00
(68)	4	3.70
(69)	6	1.46
(70)	8	0.52
(71)	10	0.33

(b) 40% ligninsulphonate + saturated dichromate + X gms ferric chloride/100 ml mix.

Mixture	Gms of ferric chloride per 100 ml mixture	Setting Times (mins.)
(72)	2	8.75
(73)	4	3.25
(74)	6	1.15
(75)	8	0.46
(76)	10	0.24

(c) 30% ligninsulphonate + 60% dichromate + X gms ferric chloride/100 ml mixture.

Mixture	Gms of ferric chloride per 100 ml mixture	Setting times (mins.)
(77)	2	16.20
(78)	4	4.01
(79)	6	1.06
(80)	8	0.55
(81)	10	0.45

(d) 20% ligninsulphonate + "40%" dichromate + X gms ferric chloride/100 ml mix

Mixture	Gms of ferric chloride per 100 ml mixture	Setting times (mins.)
(82)	2	66.0
(83)	4	4.38
(84)	6	2.18
(85)	8	2.28
(86)	10	3.30

(e) 10% ligninsulphonate + "20%" dichromate + X gms ferric chloride/100 ml mix.

Mixture	Gms of ferric chloride per 100 ml mixture	Setting times (mins.)
(87)	2	67.50
(88)	4	12.20
(89)	6	11.50
(90)	8	14.40
(91)	10	20.40

(f) 5% ligninsulphonate + "10%" dichromate + X gms ferric chloride/100 ml mix.

Mixture	Gms of ferric chloride per 100 ml mixture	Setting times (mins.)
(92)	2	12.80
(93)	4	8.00
(94)	6	13.60
(95)	8	26.30
(96)	10	54.50

Summary of physical quality of gel after gelation for $\leqslant$ 10% gels

(25) Gel bleeds when stirred

(26), (27), (28) Firm and brittle (does not pour) / Does not bleed when stirred

(29) Very loose gel, pours and bleeds when stirred

(30) Very loose gel, pours and bleeds when stirred

Comment: Best gels correspond to shortest gel times.

(31), (32), (33), (34), (35), (36) Gels are loose and light and bleed from shear of viscometer / Gels formed are soft enough to smash up when shaken strongly. / Best gel is (31) which corresponds to shortest gelation time and quality deteriorates with increasing gelation time.

(57), (58) Firm but bleeds when stirred.

(59) Very loose gel and bleeds extensively when stirred or sheared

(60), (61) Not formed

Comment: (a) Best quality gel corresponds to least gelation time.

(b) 1:½ gels are not as good as 1:1 gels in general.

(62), (63), (64), (65), (66) Gels are weakly formed, extensively sheared by viscometer and similar comments in (a) and (b) above.

(87) Light gel formed which is extensively sheared and bled by viscometer

(88) Heavier gel formed, but bleeds when stirred

(89) Heavier gel formed, but bleeds when stirred

(90) Loose gel formed which bleeds extensively when stirred

(91) Loose gel formed which bleeds extensively when stirred

Comment: (a) These 1:2 gels are slightly inferior to corresponding 1:1's at gel point but superior to corresponding 1:½'s

(b) Though they are loosely formed at best, they do set to give firm gel if allowed to stand undisturbed for long periods.

(92)
(93)
(94) Similar comments in (a) and (b) above.
(95)
(96)

The physical quality of $\leqslant$ 10% ligninsulphonate gels can be qualitatively determined in terms of shearing by viscometer, bleeding when stirred and density of gel formed at gel point.

Within a given series e.g. 1:1's, 1:½'s and 1:2's the trend in relative quality of the gels can be approximately deduced from the relative seriousness of above characteristics but would be difficult to define quantitatively. It was noticed that the length of gelation time was proportional to the degree of susceptibility to shearing and bleeding and a comparison of the gel time would provide for a convenient quantitative evaluation of physical quality of gel and their trends within a given series. An examination of the gel times support the impression from qualitative evaluation that the quality of gel is proportional to the concentration of ligninsulphonate solution used and varies in a complex (not proportional)manner with additions of ferric chloride but the best gels invariably correspond to those of shortest gel times.

The relative quality of gels between series as a whole is best evaluated from the density of gels formed, the order of quality is found to be 1:1's > 1:2's > 1:½'s.

4.3 Discussion for optimum gel mixtures in terms of least cost, quality of gel (including hardness) and nature of soil condition

The variation of gelation times for varying ligninsulphonate concentrations, ligninsulphonate: dichromate ratios and additions of ferric chloride is best summarised graphically by plotting setting times for same amounts of ferric chloride as a function of calcium ligninsulphonate concentrations. These are given in figs 18, 19, and 20.

Attempts at fitting the curves into a mathematical expression for purpose of analysis failed and mixtures of required setting time of forty minutes for the N.Z.E.D. could be selected with the aid of the figures.

A more useful way of utilising the data would be to determine for gel mixtures that optimises on a number of important criteria (a) low cost (b) gelling time of around forty minutes and (c) good physical quality in terms of sufficient mechanical strength.

The cost factor is simply proportional to the concentrations of ligninsulphonate, dichromate and ferric chloride used while the behaviour of physical quality of all gel mixtures investigated are as summarised:

(1) For all gels of > 10% ligninsulphonate solutions — These gels are always solidly formed, strong and tough. They are not easily sheared unless by large applied forces. Generally they solidify rapidly except for 20% - 30% ligninsulphonate

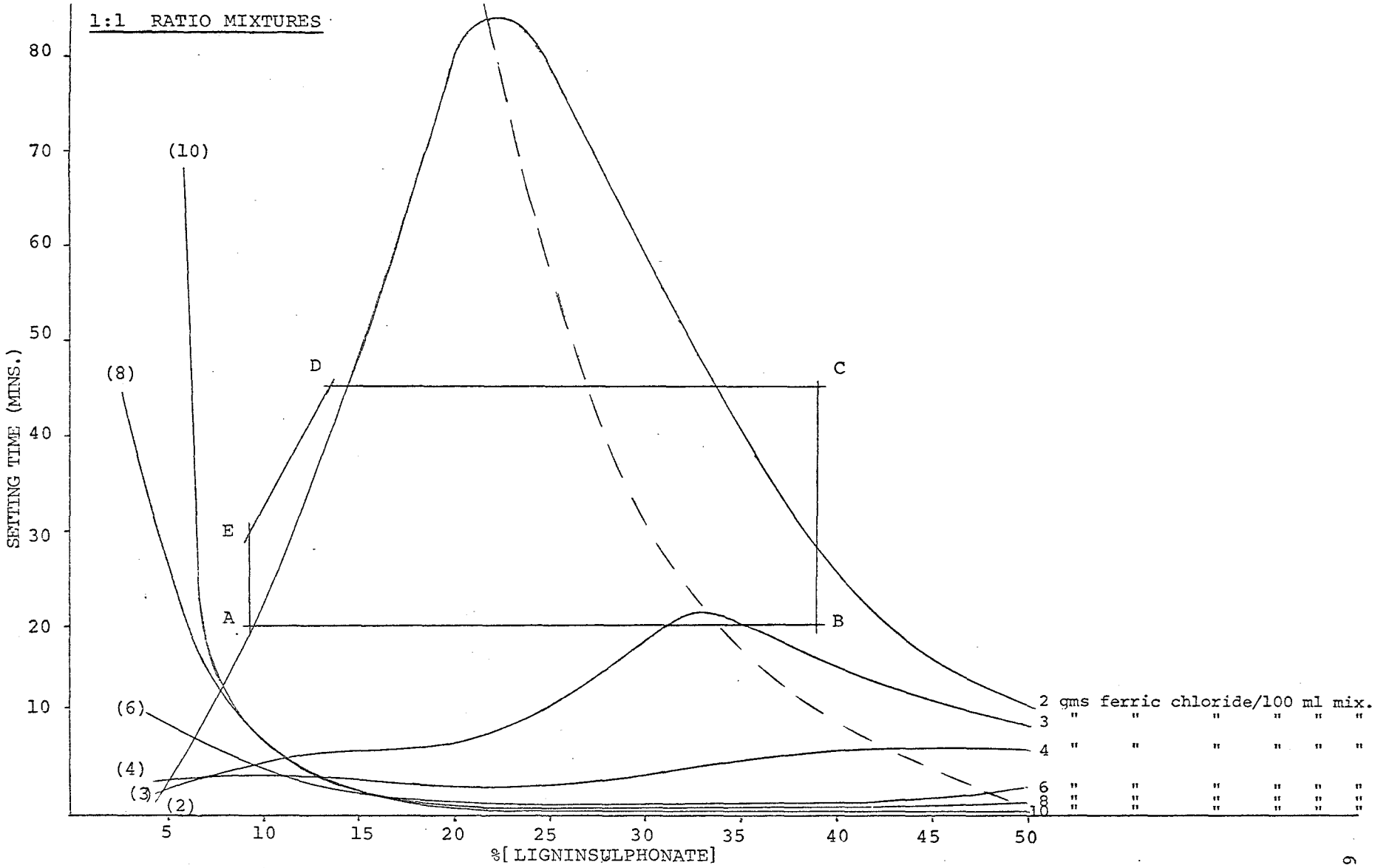


FIGURE 18: Setting times of gel mixtures of ratio, ligninsulphonate: dichromate = 1:1 and catalysed by ferric chloride.

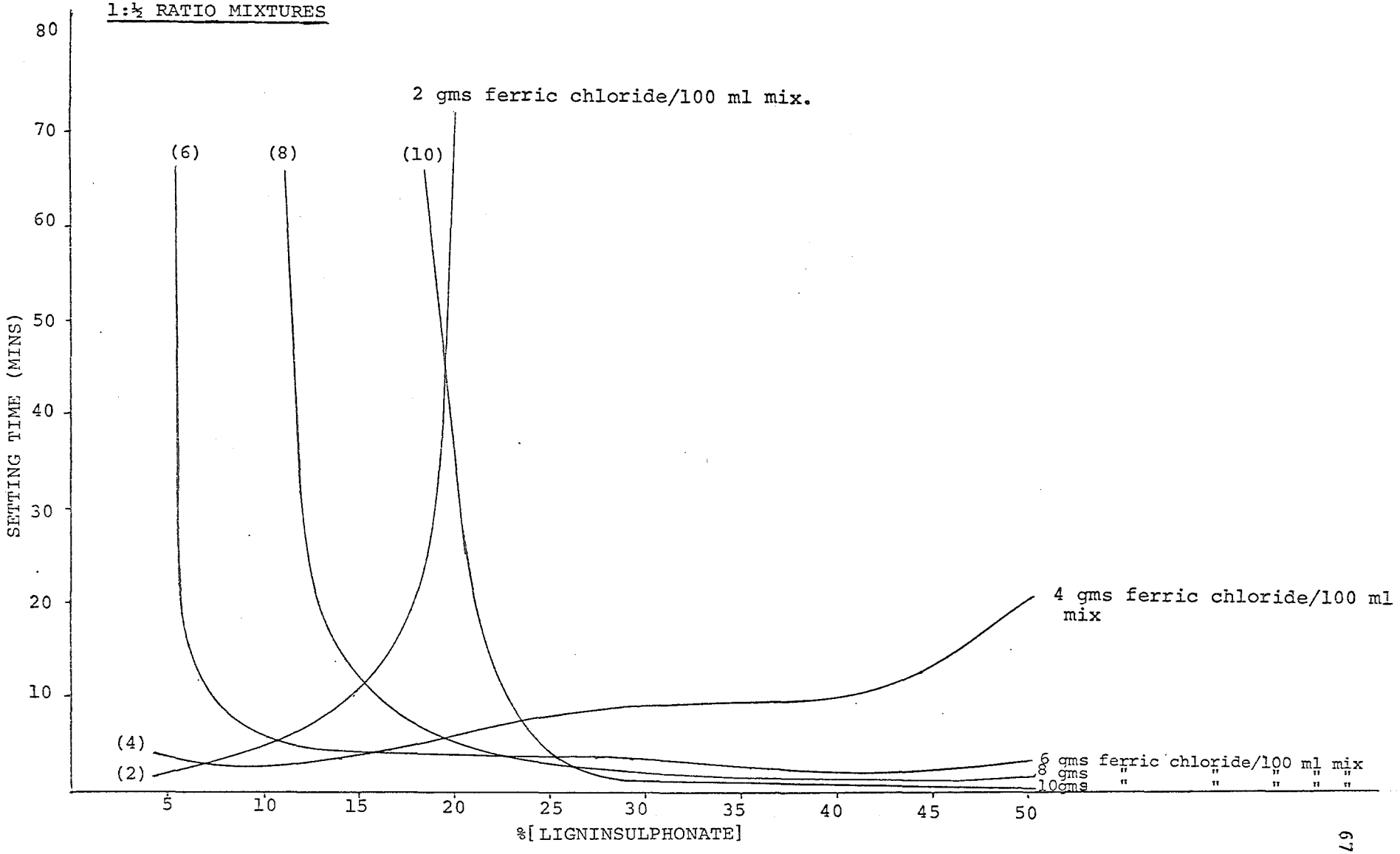


FIGURE 19: Setting times of gel mixtures of ratio, ligninsulphonate: dichromate = 1:½ and catalysed by ferric chloride.

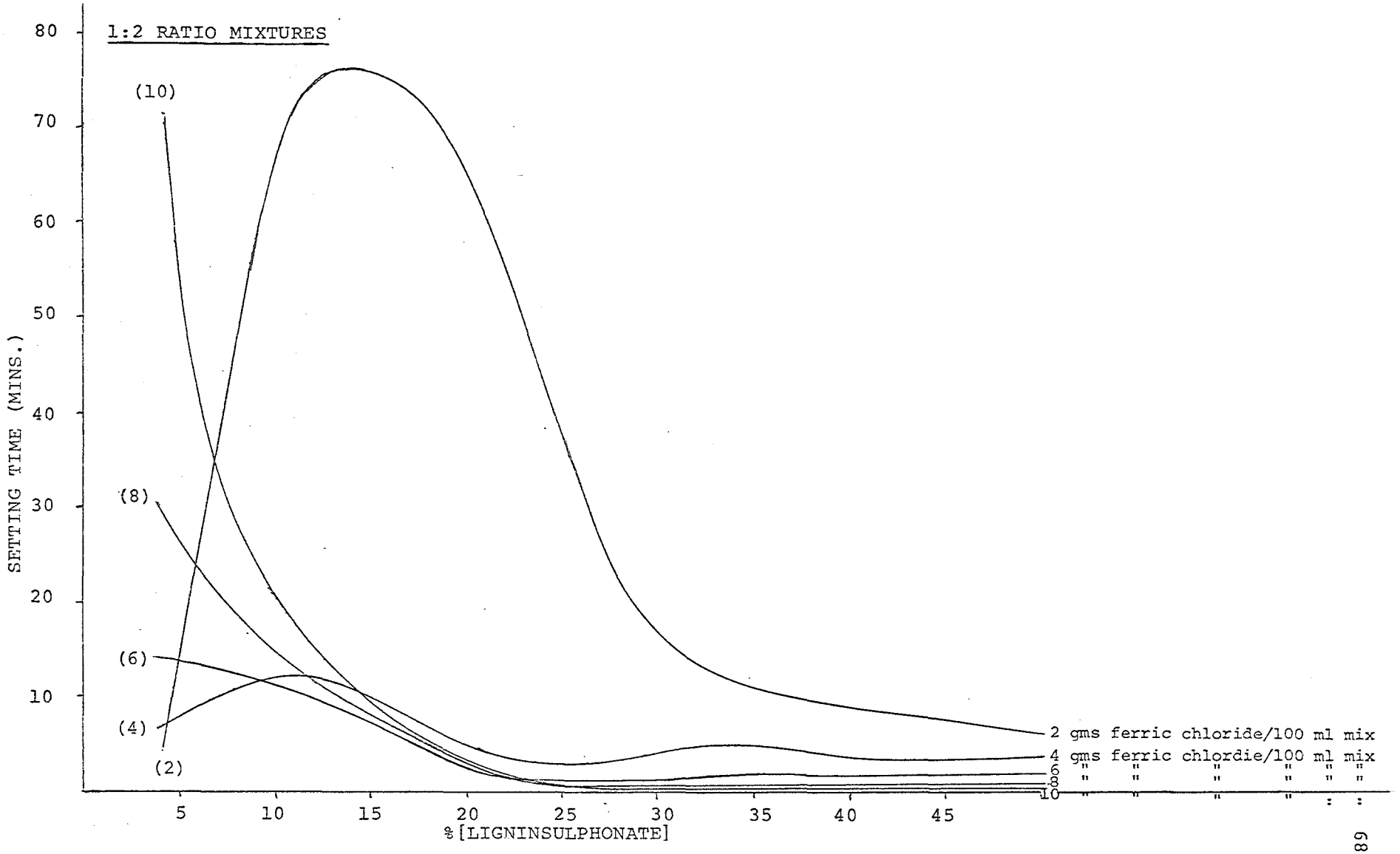


FIGURE 20: Setting times of gel mixtures of ratio, ligninsulphonate:dichromate = 1:2 and catalysed by ferric chloride.

solutions of low ferric chloride concentrations ($\leqslant$ 2 gms/100 ml mixture) which are long gelling and remain in a thick viscous state for quite a while after gelation before complete solidification sets in.

(2) For all gels $\leqslant$ 10% ligninsulphonate solutions — These gels are comparatively light and are easily sheared even by small forces. At their best they are firm and "brittle" and make good gels, otherwise they are susceptible to bleeding by mechanical disturbances after gelation, but are capable of giving a firm gel if left undisturbed for some time provided there is sufficient dichromate present as in 1:1 and 1:2 mixtures. The physical quality of these gels are dependent on the composition of the mixtures in a variable manner and could be defined along the following trends.

(a) Physical quality and hardness is primarily dependent on the concentration of ligninsulphonate solution used.

(b) Of all three ratio mixture series that gelled, the best gels were those of 1:1's followed by 1:2's and then 1:½'s.

(c) the effect of additions of ferric chloride is complex but for a given ligninsulphonate concentration and mixture ratio, it was found that the best gel strictly corresponded to the shortest gel time, deteriorating with increasing gel time.

On the basis of this data, a number of useful gel mixtures are suggested to lie within the area defined approximately by ABCDE for 1:1 mixtures, fig. 18, the boundaries are determined as follows: AB is the lower limit of gelling time allowed. This is determined by the time required to inject the grouting into the ground (which is dependent on pumping equipment used and the soil conditions). BC is the upper cost limit of ligninsulphonate concentration used. DC is the upper time limit allowed for completion of pumping of a given quantity of mixture into the ground. More important, it is also the upper gelling time limit of gels that would be expected to show a reasonably rapid rate of solidification after gelation to minimise loss of gel mixture by drainage if the gel remains fluid for a long time after. AED is the lower quality and hardness limit of a useful gel. This is determined by the concentration of the lignin-sulphonate solution and the quickness of their gelation for those low concentration gels (i.e. $\leqslant$ 10% ligninsulphonate).

Thus a large number of gel mixtures of varying properties could be selected to "fit" the requirements and problems associated with different kinds of soil. For example, a 10% gel with short gelling time readily gives a firm gel but would be expected to be susceptible to drying and leaching since its cross-linking density is light and would therefore be less suitable for excessively dry or wet porous soils. It was reported by Mr Gordon Young of the N.Z.E.D. (private communication) that difficulty was encountered in

retaining the gel after injection of an uncatalysed 40% ligninsulphonate grouting in limestone soil. The reason is thought to be due to the alkaline and porous nature of limestone. The alkalinity of the soil increases the pH of the gel mixture which either stops the polymerisation reaction altogether or slows the gelation process considerably with the result that the mixture continues to drain away after completion of pumping. Further, it could be seen from an examination of the viscosity profile of long gelling mixtures in Appendix A that slow polymerising gels characteristically retain considerable fluidity for a good while after gelation, the duration of which is proportional to the gelation time.

To take into account such varied problems not directly arising from the composition of the gel mixtures one other important property required of injection groutings in general would be that they give a rapid or sudden rise in viscosity at gel point in order that the gel would take hold in the soil immediately. As an aid to permit a more controlled selection and application of gel composition for varying soil conditions, the viscosity profiles of most mixtures investigated in table 1 are supplied in Appendix A.

Once a polymerising gel grouting administered is retained in the soil, the gel would remain permanently in the ground as it continues to harden after formation. Hardness of the gel increases even after two weeks from gelation[21].

In addition to the factors last discussed, other factors which are important to the N.Z.E.D. are physical, chemical and electrical stability and the electrical conductivity of the gel. The following experiments are intended to throw light on these aspects for the gels already described and for gels to which have been added copper (II), manganese (II), chromium (III) and aluminium chlorides. These additives have a profound effect on the progress of the gelation reaction as described in Chapter V.

4.4 Hardness of gel contributed by additions of hydrochloric acid and metal chlorides

The hardness of these gels were qualitatively evaluated by the ease with which the gel could be broken up after gelation and the speed with which the gel transforms completely to solid state after gel point. Normally the gel at gel point is still a thick viscous state before it solidifies. The longer a gel takes to harden up the softer in texture would be expected of the gel.

The mixtures studied were made up of the following compositions with a 50% ligninsulphonate solution:

(a) 30 mls of 50% ligninsulphonate + 6.6 mls of "50%" dichromate + X mls conc. HCl (10.4 M/l) + (10-X) mls water
= 46.6 mls total.

(b) 30 mls of 50% ligninsulphonate + 6.6 mls of "50%" dichromate + y moles of metal chloride + 10 mls water
= 46.6 mls total.

Table 2: Hardness of gel contributed by hydrochloric acid and metal chlorides.

(a)

Moles of Hydrochloric acid	Gelling Time (mins.)	Hardness of gel at gel point	
0.0000	29.00	Gels are viscous at gel point, takes 1-2 mins. to solidify.	Good, moist gels with little or no bubbles entrapped.
0.0104	14.50		
0.0208	5.40		
0.0312	3.38		
0.0416	2.50	Gels begin to deteriorate with increasing HCl additions.	Good, dry but spongy with tiny bubbles entrapped.
0.0520	2.95		
0.0624	3.18		
0.0832	5.25		Frothy but firm and dry.
0.1040	31.00		Frothy and in a degraded viscous state

(b)

Moles of aluminium chloride.	Gelling Time (mins.)	Hardness of gel at gel point	
0.00346	17.35	Gels are viscous at gel point, takes 1-2 mins. to solidfy.	Hardness of gels is parallel to those of HCl additions on basis of equivalent moles of H^+ released by $AlCl_3$.
0.00749	11.50		
0.01042	8.85		
0.01386	9.00		
0.01733	7.00	All gels are good and firm and hardness increase with increasing additions of salt.	Hardness of gels is greater than HCl additions.
0.02079	7.30		
0.02773	6.80		
0.03467	6.20		

(c)

Moles of ferric chloride	Gelling Time (mins.)	Hardness of gel at gel point	
0.00346	26.25	Gels are viscous at gel point, take about 2 mins. to solidify.	Gels are harder than HCl addns on basis of equivalent H^+ released
0.00694	8.25		
0.01039	1.50		
0.01386	<0.50	Gels are almost solid at gel point	Gels are harder than similar $AlCl_3$ addns.
0.01733	<0.30		

(d)

Moles of cupric chloride	Gelling Time (mins.)	Hardness of gel at gel point	
0.00520	2.25	Gels are almost solid at gel point, take no longer than ½ minute to solifify.	Gels are harder than similar addns of $AlCl_3$.
0.01039	0.50		
0.01559	0.30		

(e)

Moles of manganous chloride	Gelling Time (mins.)	Hardness of gel at gel point	
0.00260	10.95	Gels solidify almost at gel point and take about ½ minute to solidify.	Gels are harder than similar addns of $AlCl_3$.
0.00779	5.85		
0.01298	4.30		
0.01559	3.90		
0.01820	3.78		
0.02339	3.23		
0.02859	2.85		

(f)

Moles of Chromium Chloride	Gelling Time (mins.)	Hardness of gel at gel point	
0.00347	22.50	Gels are viscous at gel point, take 1-2 mins to solidify.	Gels are harder than similar addns. of $AlCl_3$.
0.00693	13.80		
0.01039	11.45		
0.01386	9.90		
0.01733	8.80		
0.02079	9.55		

Generally hardness of gel increaseswith increase of metal chlorides added and though the hardness of gels appear to vary at gel point, once fully solidified they seem to display little difference.

Cupric chloride and ferric chloride which gave very short gelling times produced a much harder gel at their gel points than other metal chlorides for similar moles of salt added while gels with hydrochloric acid additions always gave the softest gels.

These trends were similarly observed by Akahane and Yano[8] with penetrometer measurements.

Since the differences in hardness with metal ion additives exhibited in the immediate post gelation period do not remain after an extended time, hardness based on the nature of metal chlorides added would be unimportant. The high positive charge on the metal ions probably serves to attract negative groups of the lignin molecule together and in this manner contribute to additional strength of the gel.

4.5 Chemical stability of gels

The consumption of dichromate was shown by Hayashi[21] to progress into the solid gel state. This was presumably due to continued generation of crosslinks as well as oxidation of ligninsulphonate substrate and in the long run the degradative nature of these oxidative processes would be detrimental to both the physical and electrical stability of the gel.

From an examination of table 2 and for additions of hydrochloric acid, it is evident that an excess of hydrogen ions cause a deterioration of the gel. For example, at 0.104 moles, the gel obtained is frothy and its gelation somewhat prematurely terminated together with large production of heat. The hydrogen ions can be described as either directly or indirectly promoting the oxidative degradative side reactions which destroy the sites of crosslinking and inhibiting gelation.

It is clear that hydrogen ions would not make a good promoting agent for the polymerisation compared to the metal chlorides, that a less acidic reaction mixture would be best as the gel would be subjected to a minimum of chemical degradation, and that the best metal chloride promoters would be one that has minimal hydrolysis. Cupric chloride which has high catalytic activity and show little hydrolysis in ligninsulphonate solution (Chapter V) would seem to be most suitable in this respect.

4.6 Conductivity and electrical stability of the gel

In spite of the success of the ligninsulphonate gel tested in reducing ground resistance in Japan, no extensive data has yet been uncovered about the conductivity properties of these gels. Conductance measurements were therefore made on all 1:1 gels promoted by ferric chloride, copper chloride and aluminium chloride as catalysts. The 1:1 gel mixtures made were of similar compositions to that for viscosity measurements in Chapter III i.e. 50%, 30% and 10% ligninsulphonate gels each containing 2,4,6,8 and 10 gms of metal chloride per 100 mls mixture. The resistance of the gels were monitored with the A.C. transformer ratio arm inductance bridge for two hours and their dependence with time were presented in Appendix B.

In general there is little difference in the initial resistances of comparative concentrations of gels containing various metal chlorides but on the whole, copper chloride distinctly gave the best results in that their gels show the smallest rate of increase in resistance over a long period of time. Aluminium chloride which relies on hydrogen ions released in "promoting" the gel (Chapter V), showed an inclination to rapidly raise the resistance of the gel over time. The conductivity of the catalysed gels appeared to be improved slightly with increase in concentration of additive but for excessively large additions of ferric chloride i.e. 10 gms/100 mls mixture, a sudden rise in resistance occurs after some time for some gel concentrations. Such gels would be unsatisfactory as a conductor and would be ruled out on the basis of cost anyway.

A similar experiment but on a smaller scale was conducted on a number of gels catalysed by ferric chloride in which the resistance of the gels was measured using an earth test mega for varied concentrations of reagents. This experiment was conducted by Mrs Janet Jackson of the N.Z.E.D. in correlation with this work.

A cell consisting of two aluminium plates of 5 cm wide and 10 cm long, placed parallel and 1 cm apart was constructed, diag. 21. Each of the plates was suspended from a vertical threaded bolt which hung from two horizontal rods. The rods were placed across the top of a container and by turning the screws, the electrodes could be adjusted to be immersed in the gel mixture up to a 2 cm height mark.

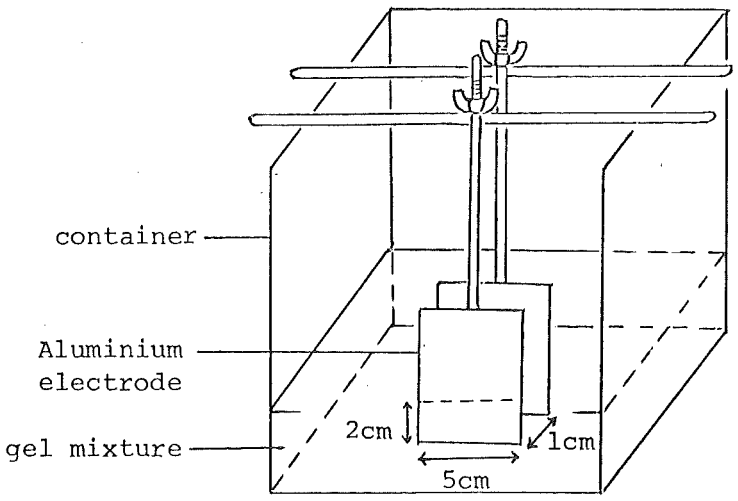


FIG. 21: Aluminium electrode cell for measurement of resistance with an earth test mega.

Table 3: Resistance of gel mixtures catalysed by ferric chloride and measured with an earth test mega.

Mixture	ligninsulphonate solution	Dichromate solution	Gms of ferric chloride taken	Resistance (Ω)
(1)	40 gms in 300 mls = $13\frac{1}{3}$%	40 gms in 100 ml = 40%	12	38
(2)	60 gms in 300 mls = 20%	40 gms in 100 ml = 40%	12	39
(3)	80 gms in 300 mls = 26%	40 gms in 100 ml = 40%	12	39
(4)	100 gms in 300 mls = $33\frac{1}{3}$%	40 gms in 100 ml = 40%	12	39
(5)	60 gms in 300 mls = 20%	80 gms in 100 ml	12	38
(6)	60 gms in 300 mls = 20%	85 gms in 100 ml	12	37
(7)	60 gms in 300 mls = 20%	85 gms in 100 ml	24	30

The mixtures in table 3 were prepared as follows taking mixture (1) as an example: 40 gms of ligninsulphonate was dissolved in 300 ml water, 40 gms of dichromate was dissolved in 100 ml water together with 12 gms of ferric chloride. The ligninsulphonate and dichromate-ferric chloride solutions were mixed to give a total of 400 mls. The absolute resistance of the gel mixture was measured after two hours of reaction.

The results in Table 3 show that the resistance of the gel is relatively insensitive to the strength of lignin and dichromate used at these concentrations and that a reduction in ligninsulphonate concentrations actually resultsin a decrease in resistance. A lower concentration of ligninsulphonate is obviously an advantage both in terms of cost and conductivity and since the resistance of the gel is quite insensitive to the concentration of dichromate used, a lower dichromate solution could also be used to minimise cost. As for the ferric chloride it is considered not worthwhile in terms of cost to double the amount of salt used as there is little difference between a gel of 37 ohms and 30 ohms for the purpose of a conductor.

The average resistance of the gel mixtures catalysed by the ferric chloride was 35 ohms giving an average resistivity of 350 cm Ω.

CHAPTER V

KINETICS OF GELATION OF CALCIUM LIGNINSULPHONATE CATALYSED BY METAL CHLORIDES

5.1 Introduction

A lot of work has been conducted on the uncatalysed gelation of ligninsulphonate by dichromate but little is still known about the mechanism and kinetics of the reaction catalysed by additives. In a further investigation on the feasibility of using ligninsulphonate as a soil treatment chemical, Akahane and Yano[8] performed some preliminary studies on the promoting effects of metal salts and the reaction conditions under which gelation occured. The salts used include a large number that have been known to be catalytically active in well known reactions and which might be thought to be also active in the gelation of ligninsulphonate.

Their results showed that the salts of aluminium, iron, copper, nickel, silver, zinc and calcium did promote the gelation and among these the first three were most effective and were treated with greater importance. Copper chloride showed the greatest effects and only a small quantity was sufficient to produce a profound reduction in gelation times. Aluminium was less effective than copper but more active than ferric chloride for small amounts and was otherwise the least effective of all three. The gelation

times with aluminium chloride showed a minimum for large additions of the salt. Ferric chloride exhibited the least activity for small concentrations but improved rapidly for large amounts.

Tests were also made by Akahane and Yano on the combined effects of the above three catalysts but they showed no appreciable difference from using the salts independently. Unlike the chlorides, the sulphate salts of the additives generally caused the formation of calcium sulphate sedimentation and resulting in reduced promotion effects while the hydrolysis of the chloride salts especially that of iron and aluminium in aqueous solution produced a large shift in the pH of the ligninsulphonate-dichromate mixture from its near neutral property. The effects of pH on the gelation reaction was still uncertain.

5.2 Oxidative Polymerisation of Ligninsulphonate Catalysed by Promoters/Additives

The condensation-dimerisation of ligninsulphonate was described by Hayashi to be the major reaction in the gelation of the polymer with large molecular weights (> 2,900). The evidences in Chapter III showed that the truth was far from complete and that more than one mechanism contributed to gelation in which the integration of chromium atoms into the gel is not necessarily involved. That small size molecules are actually capable of gelling and could do so with ease would mean that Hayashi's mechanism is not important with Discon and that a second

mechanism which is as favourable, exist and whose active sites of gelation are more numerous than the catechol groups.

Dichromate is a strong oxidising agent and it is not difficult to conceive that a redox polymerisation process is a most attractive alternative. The particular success of copper and ferric chlorides reported by Akahane and Yano in promoting the gelation points to a classic case of an oxidation-reduction process involved in the polymerisation. As the other oxidation-degradative processes are generally slow, the chromium (III) ions produced are largely the result of such redox polymerisation.

In the dehydration coupling mechanism proposed by Tanaka and Senju[21], the coupling takes place directly between benzene nuclei, Fig. 4, in which the dichromate reacts just as an oxidant and does not take part in the crosslinks directly among ligninsulphonate macromolecules. This particular mechanism has been rejected by Hayashi but a similar sort of redox reaction as yet unknown must be operative and would be dominant in a catalysed mixture. This belief is supported by the experiments on the role of metal chlorides as promoters which will be reported.

5.3 Mechanism of Oxidative Polymerisation, Catalysis, and Electron-Transfer Reactions

Like many oxidation-reduction reactions, the oxidative polymerisation could be described as an electron-transfer reaction in which electrons are transferred from the reducing agent to the oxidising agent.[26] The reduction

of chromium (VI) to chromium (III) would involve the transfer of three electrons per dichromate ion and the process is expected to occur in stages and involving a series of complex steps, each of which require the transfer of one electron.[27] This is possible as the chromium (VI) ion being a transition metal ion would be expected to have a number of relatively stable oxidation states differing by one equivalent.[26]

In any overall process[27] where two or more electrons are transferred, it is often possible for catalysis to be brought about by introduction of a species having two valence states differing by unity and of energy levels close to each other. e.g. Cu^{+} - Cu^{2+}, Fe^{2+} - Fe^{3+}. During the process the catalyst invariably enters into chemical union by complex formation with the substrate (here ligninsulphonate) to form intermediates or products of the reaction with regeneration of the catalyst. The factors which are expected to determine the activity of an electron-transfer metal ion catalyst include the following:

(1) Magnitude of reduction potential of metal ion.

The role of a catalyst in a reaction is to produce a new reaction pathway of lower free energy of activation and for an electron-transfer agent to do this, it is necessary that the reduction potential of the complexed metal ion be small and to correspond to oxidation state couples differing by one equivalent. Reduction potentials corresponding to the transfer of two or more electrons would require the use of a large number of intermediate

steps and would render the catalyst not much more efficient than the dichromate itself.

Transition metals which exhibit a large number of oxidation states generally play the role of electron transfer catalysts in redox reactions. Though the reactivity of the metal aquo complex is determined by parameters which are different from those of its other complexes nevertheless the non-aquo complexes[28] do follow a trend parallel to that of the aquo complexes and the relative electron-transfer capacity and efficiency of a complexed metal ion are indicated from the standard reduction potential of the metal ion. The reduction to metal ions of common transition metal are included in table 4 below.

Table 4: Standard reduction potentials of some common transition metal ions

Ion-Electron Half Equation	E^{o}, Volts
$Cu^{2+} + e \rightleftharpoons Cu^{+}$	0.158
$Fe^{3+} + e \rightleftharpoons Fe^{2+}$	0.770
$FeO_4^{2-} + 8H^{+} + 3e \rightleftharpoons Fe^{3+} + 4H_2O$	1.900
$Mn^{3+} + e \rightleftharpoons Mn^{2+}$	1.510
$MnO_4^{-} + 4H^{+} + 2e \rightleftharpoons Mn^{3+} + 2H_2O$	1.208
$MnO_4^{-} + e \rightleftharpoons MnO_4^{2+}$	0.568
$MnO_4^{-} + 8H^{+} + 5e \rightleftharpoons Mn^{2+} + 4H_2O$	1.491
$Cr^{3+} + e \rightleftharpoons Cr^{2+}$	-0.410
$Ag^{2+} + e \rightleftharpoons Ag^{+}$	1.987

Metal ions of iron, copper and chromium which have oxidation state couples of fairly small energies are expected to make good electron transfer agents while all other metal salts mentioned earlier including manganese and silver which either reduces to solids or possess high reduction potentials would have small catalytic activity. This was roughly as observed by Akahane[8] with the exception of aluminium chloride which is never known to be an electron transfer agent in aqueous medium and yet showed unexpected activity.

(2) Stability of metal ion catalyst-complex with ligninsulphonate substrate.

Assuming for simplicity, the catalyst M^{n+} first approach the active site, complexes with it and then oxidises the active site. The complex then decompose to release the $M^{(n-1)+}$ ion which migrates over to the dichromate to be oxidised back to M^{n+}.

For the catalyst to be efficient, it is therefore important that the metal ion forms sufficiently strong bonds to give a large concentration of complexes and yet not so strong as to prevent it from readily coming away from the oxidised active site. Conductometric titrations were conducted by Hayashi[29] for the chelation with ligninsulphonate and the log of the stability constants calculated were 5.30 (Fe^{3+}), 2.50 (Cu^{2+}), 3.40 (Cr^{3+}) and 1.09 (Co^{2+}). Assuming the large activity of copper reported as indicating a stability constant of about 2.50 as the optimum value, then any stronger or weaker complexes

with lignosulphonate would be expected to show less catalytic activity.

(3) Kinetic inertness of complex

Cobalt (III) and chromium (III) form a large number of complexes which are not only stable but also kinetically inert,[30] the ligand displacements of these complexes are very slow. Since the metal ion would not be expected to remain a free ion in solution as the reaction mixture contains various other anions, the decay of the complex would involve the displacement of the ligninsulphonate ligands by these other anions present, and if this process is part of the slow step, the kinetic inertness of the metal ion catalyst would in turn be expected to influence the polymerisation rate.

5.4 Kinetic Studies Performed on the Oxidative Polymerisation of Ligninsulphonate by Dichromate and Catalysed by Selected Promoters.

In the following experiments we have pursued the kinetic studies from where Akahane left off by attempting to resolve both the contribution to setting rates by hydrogen and metal ions, the role and capacity of the latter as electron-transfer agents and establishing for the order and rate equation of the catalysed reaction.

It is noticed that the chromium (III) ion has comparable reduction potential to those of copper and iron

but was reported by Akahane to be only slightly active. This would indicate that the catalytic efficiency of electron-transfer agents are also controlled by other factors as described in last section and we would attempt to identify for the rate determining factor(s) 'peculiar' to each metal ion catalyst in the polymerisation.

Aluminium chloride is distinctly anomalous among all the salts reported by Akahane in that it has a high reduction potential of -1.706 and its reduction requiring the transfer of three electrons as there are no other stable oxidation states between Al^{3+} and Al^{0}, yet it showed an activity comparable to copper and iron salts. The demonstrated catalytic activity of aluminium chloride is usually associated with its Lewis acid nature as an electron pair acceptor but this occurs only in organic solvent media e.g. in the Friedel-Crafts Alkylation and Acylation. In aqueous solution however, aluminium chloride is hydrolysed extensively to produce an Al(III) aquo ion with release of hydrogen ions. As the Al(III) aquo ion is unlikely to accept electrons easily, the activity of aluminium chloride is possibly a hydrogen ion concentration effect.

For the transition metals iron and manganese which have more than two stable oxidation states, it is possible that more than two oxidation states are used in their function as redox catalyst in electron transfer to calcium ligninsulphonate. Kinetic investigations may help to resolve this directly as the rate for an oxidation-reduction

that involves more than two species or two or more equivalent changes would not be first order in the catalyst.[26]

The following additives were selected for study in our investigations to throw some light into these areas of interest, they were: hydrochloric acid, aluminium chloride, ferric chloride, copper chloride, manganese chloride and chromium chloride.

5.5 Reagents Used

The purification of commercial calcium ligninsulphonate (Discon) which contain both inorganic and organic impurities presented unique difficulties due to the polydispersity of the compound. A good degree of purification could be achieved by subjecting a solution of ligninsulphonate to ion-exchange treatment[16,31] to remove the inorganic materials and dialysis through denitrated nitrocellulose membrane of low porosity. Other procedures have also been employed by various workers but in general all these methods require extended time to perform and are not of sufficiently large scale to yield the amount of purified ligninsulphonate required for our experiments.

The unpurified compound was used instead and we assumed that the effects of impurities would be constant for a given concentration of ligninsulphonate solution. We also employed technical grade sodium dichromate making the same assumption

5.6 Temperature Control

It is appreciated that reaction rates of any reaction are dependent on temperature, the effects of which were found to be profound for the catalysed gelation of calcium ligninsulphonate. The viscous nature of the polymerising system and the strongly exothermic nature of some mixtures made temperature control extremely difficult but some attempts at temperature control of the initial state of the system were made by immersion of small test samples in a thermostated tank whenever possible.

5.7 Experimental Techniques Employed

The determination of the rate law of the polymerisation reaction involves establishing for the order and rate constant of the reaction. Experimentally the general approach is to measure the reaction velocity for various concentration of reactants with time. For polymerisation reactions the problem is one of finding a suitable method of monitoring the gelation or setting time of the reaction.

The best method of doing this was to determine for the viscosity of the gel mixture with time. Considerable difficulty was encountered in the early part of the project in finding for a satisfactory viscometer over a wide range of viscosities which occured (refer Chapter II). Initial attempts at kinetic studies were therefore involved with finding for other reliable methods of monitoring the progress of the polymerisation and it was hoped that

their measurements might be related to the gelling times. Since the gelation process involved the reaction mixture transforming from an initial liquid to a final solid or gel state, the most suitable methods were expected to be those that do not require disturbance or removal of successive samples from the reaction mixture. Three methods which were available to us and appeared most likely to succeed were investigated, they were pH measurements, electrical conductance measurements and viscosity measurements.

(a) pH measurements.

High concentrations of hydrogen ions would be consumed by the oxidising action of the dichromate and if the side reactions of general oxidation are minor, the rate of change of hydrogen ions or pH would, in the main, be characteristic of the gelling reaction and either the rate or amount of hydrogen ions used would be expected to be proportional to the rate of gelation. The concentration of hydrogen ions in a gelling mixture is easily followed with a pH meter.

(b) Conductance measurements.

Preliminary experiments on conductance measurements on the ligninsulphonate gels showed that the electrical conductance of a polymerising solution did in fact vary with time. Regarding the conductance as due to contribution from the active components in calcium lignin-sulphonate, hydrogen and dichromate ions, the consumption of these ions together with progressive interlocking of these materials into a less mobile gel matrix would be

expected to result in a fall of electrical conductance and the total change in conductance between initial and infinite time could be taken to be proportional to the gelation rate. Otherwise, we may expect the sudden solidification on gelation to be revealed in the conductance (and pH) curves perhaps as some abrupt decrease in their rates of change, from which the gelling time could be deduced.

Since the conductance is likely to be a function of the concentration of active species in the system, we attempted to analyse the conductometric data using the usual integrated rate law and initial rates method by taking the rate of reaction to be proportional to the rate of change of conductance.

i.e. $C = C_k + C_{variable}$, C = conductance

$$\therefore \frac{dC}{dt} = \frac{d(C_{variable})}{dt}$$

$$\frac{dc}{dt} = k[\text{Ions}]^n \text{ , c = conc. of ions.}$$

Assuming Ion conc, $c \propto C$

$$\text{then, } \frac{dc}{dt} = \frac{dC}{dt} = k[C-C_\alpha]$$

(c) Viscosity measurements.

The gel time is an important parameter that is essentially a function of the rate of polymerisation and as shown in Chapter III, the gel point of a polymerisation may be directly

derived from the rheogram of a gelling mixture using a torsion wire viscometer. It is desirable to establish for a relationship between the gelling times and the conductance and pH measurements. For example, the gelling times could be shown to always occur at some fraction of change in conductance or pH from initial to infinite times and the latter measurements could have provided for a more convenient approach for determination of rate of polymerisation. Unfortunately as will be seen from typical results, no such correlation was evident.

5.8 Experimental Determination of Order and Rate Law of Polymerisation of Ligninsulphonate by Measurement of pH with Time

The pH of a gelling solution was monitored by the use of a glass electrode coupled to a convectional pH meter which has a continuous chart recorder output. Measurements were recorded over two hours when the pH change was found to have become small.

A number of experimental difficulties were encountered. The long term stability of the pH meter was not found to be satisfactory. The meter drifted with time and spot checking or repeated recalibration was not possible with the electrode in a polymerising gel. As with conductance measurement, it was found that the condition of the electrode was all important in getting reproducable results due to the effects of absorbed dichromate ions on the glass walls. The gel mixture also tended to diffuse into the

membrane of the glass electrode if used for long periods and solidifying in it. The glass electrode was cleaned with a permanganic acid solution for thirty minutes but such drastic treatment resulted in further destablisation of the electrode and the solid gel lodge in the membrane was never fully removed despite the cleaning measures.

In spite of these difficulties some pH measurements have been made on gel mixtures catalysed by ferric chloride and other additives. Generally the curves showed the basic shape of an uncatalysed mixture as obtained by Hayashi[4] of an initial rapid rise followed by a slowing down of rate of change.

An examination of the graphs showed that the pH readings do not lend themselves easily to kinetic analysis over an extended time of reaction. The pH of all gel mixtures gave an initial delay in the electrode response for at least ten seconds and the initial pHs could not be determined.

The curves invariably showed themselves to increase in an oscillating manner, suggestive of some oscillating reaction from diffusion control. Typical pH curves are illustrated in fig. 22.

5.9 Experimental Determination of Order and Rate Law of Polymerisation of Ligninsulphonate by Measurement of Conductance.

The conductance measurements showed that the change of conductance given by $\Delta C = C_{t=\infty} - C_{t=0}$ varied in a complex

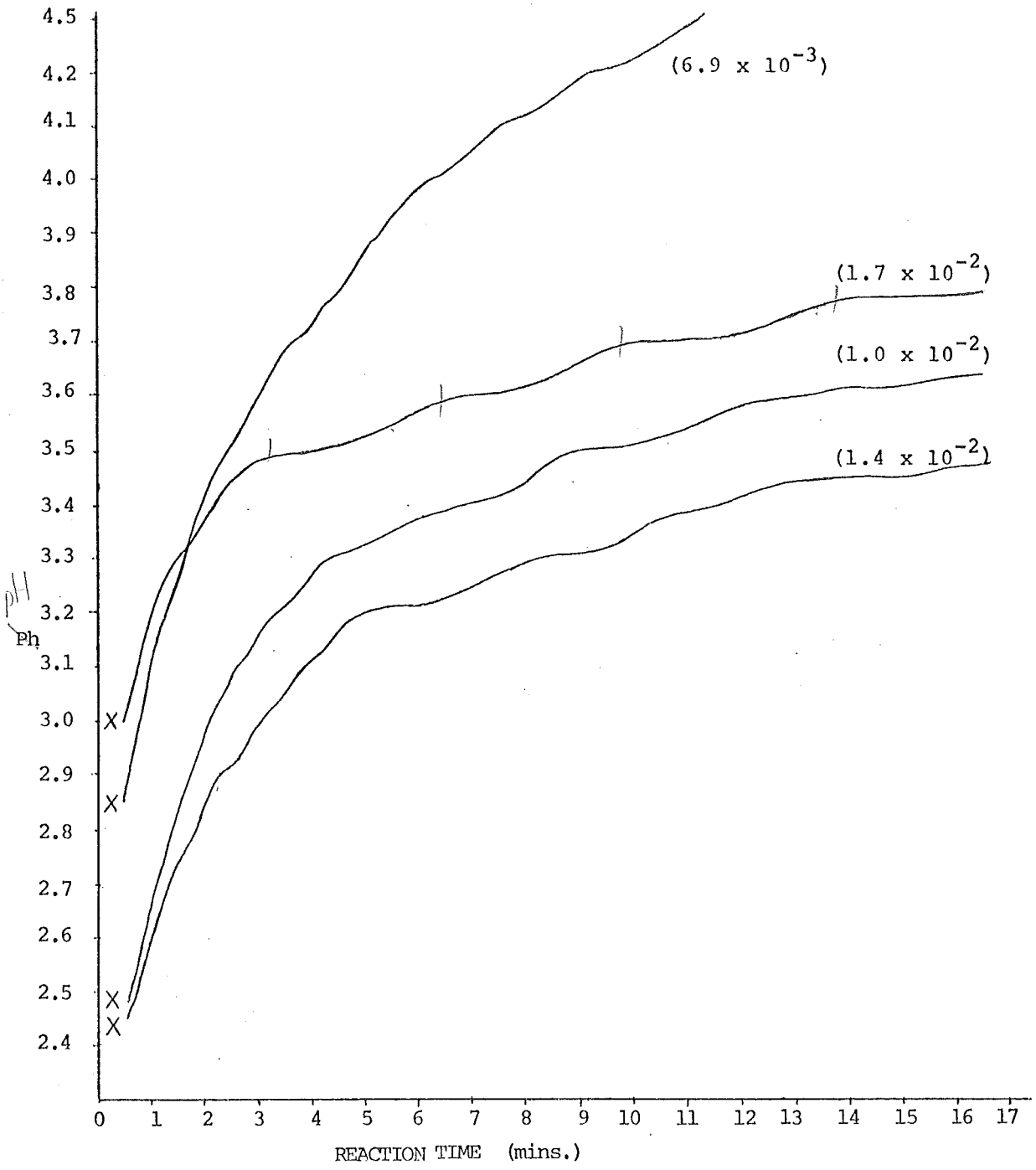


FIGURE 22: Typical ph measurements of gel mixtures containing 30 mls of 50% ligninsulphonate + 6.6 mls of "50%" dichromate + 10 mls water + (y) moles ferric chloride. "X" = delay in response of pH readings

manner with respect to composition of mixture. A simple correlation between initial rate given by $\frac{d(\frac{C}{Co})}{dt}$ and reciprocal setting time was sought but a plot of the two parameters, Fig 23, gave a random distribution denying a simple relationship between them. As the conductance change is believed to be closely related to the kinetics this result could probably be due to the orders at initial reaction not being the same as that at gelation. The conductance curves typically featured a distinct "knee" after an initial rapid rate of change of conductance. Plots of such curves of 30% ligninsulphonate, fig. 24 clearly demonstrated that the characteristic feature of the knee is not the result of "freezing" of material at gelation and this also ruled out the use of conductance measurements as a means of determining for gelling times.

The reaction order was determined using the integrated rate law by assuming that the polymerisation of lignin-sulphonate is first order with respect to ionic species and its rate expression is given by

$$\frac{d(\frac{1}{R} - \frac{1}{R_\alpha})}{dt} = -k(\frac{1}{R} - \frac{1}{R_o}); \quad R_o = \text{initial conductance}$$

R_α = conductance at infinity

$$\therefore \frac{d(\frac{R_\alpha - R}{R_\alpha R})}{(\frac{R_\alpha - R}{R_\alpha R})} = -kdt$$

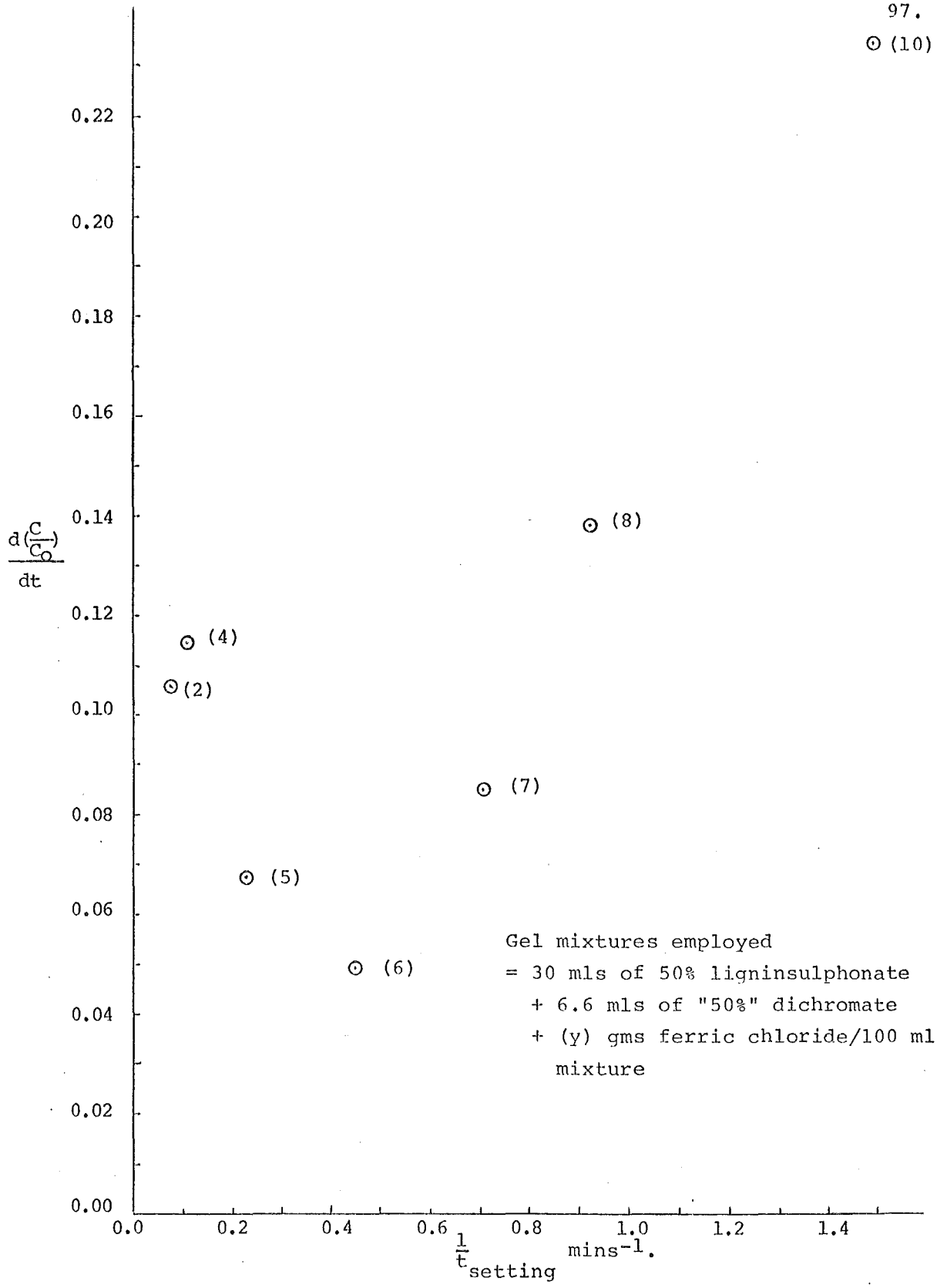


FIGURE 23: Plot of initial rate, $d(\frac{C}{C_o})/dt$, as a function of reciprocal setting time for a 50% ligninsulphonate mixture catalysed by varying amounts of ferric chloride.

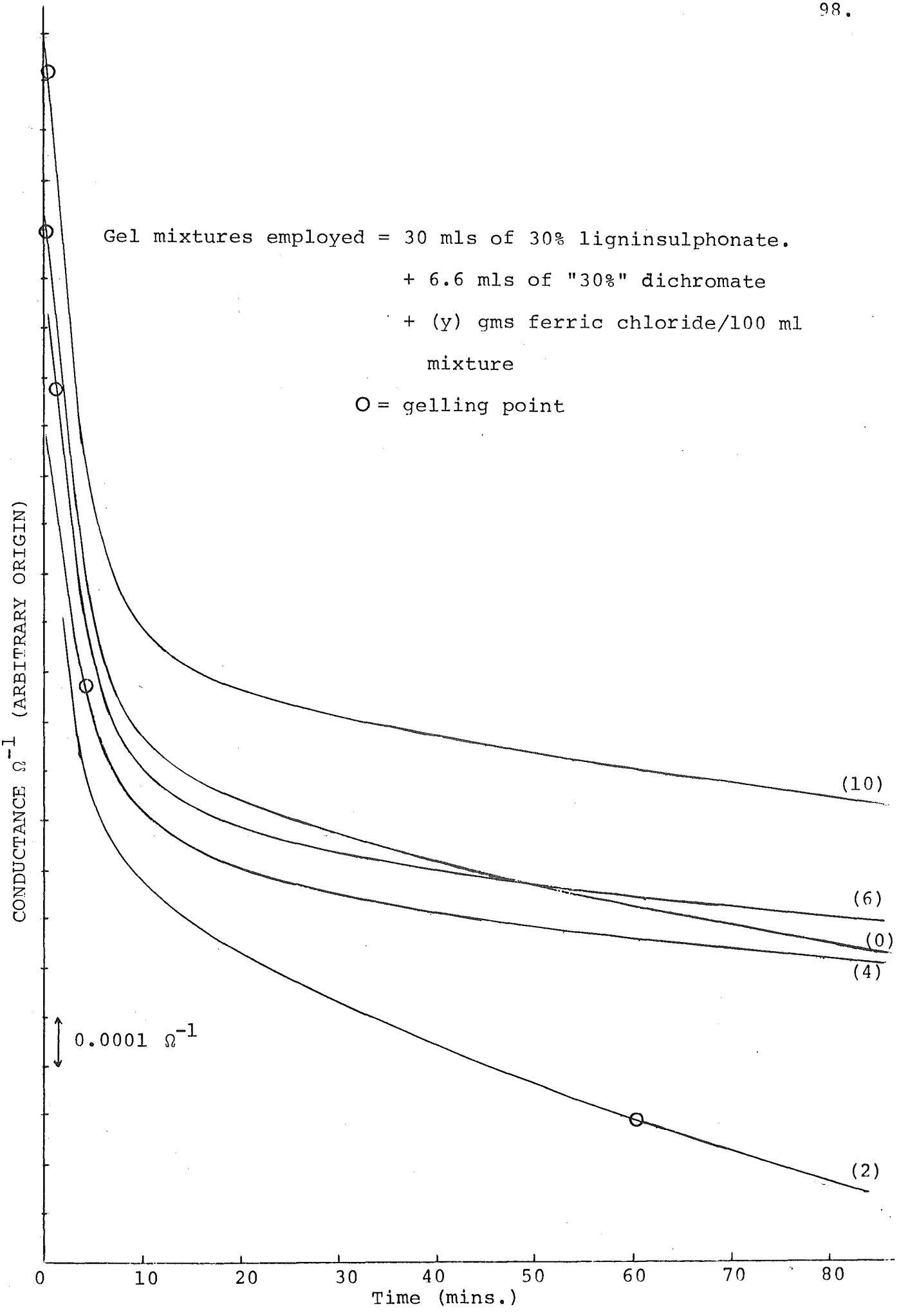


FIGURE 24: Conductance curves of 30% ligninsulphonate gel mixtures in relation to their gelling points.

Integrating,

$$\therefore \quad \ell n\left(\frac{R_\alpha - R}{R_\alpha R}\right) = - kt + \text{constant}$$

A plot of $\ell n\left(\frac{R_\alpha - R}{R_\alpha R}\right)$ versus t would give a straight line of slope k for first order in ionic concentration. R_α is taken as that resistance after end of two hours reaction.

Both the uncatlysed and catalysed gelation were investigated on a mixture of 10 mls of 50% ligninsulphonate plus 2.2 mls of "50%"dichromate and another with 2 gms of ferric chloride per 100 ml mixture. Graphical plots of $\ell n\left(\frac{R_\alpha - R}{R_\alpha R}\right)$ versus time showed that neither were first order in ionic concentrations. Similar analysis for second and third order also proved fruitless.

The electrical conductance is a reasonable measure of the average concentration of all ionic species present at a given time. In a complex reaction as gelation where new ionic species are also being generated and partly reconsumed, the rate of change of conductance could probably be controlled by other factors as well, other than a simple consumption of reagents. Under such conditions it was not surprising that the analysis of conductance by integrated rate law failed to reveal any simple chemical kinetics. Electrode capacitance determined during the course of conductance measurement showed progressive changes with time but their interpretation was also not successful.

Due to the uncertain stoichiometry of the reaction mixture with time, the detailed analysis of such a complicated reaction by the above approach would indeed be difficult. The measurement of initial rates of change of conductance would overcome this difficulty as quite a well defined initial starting composition could be determined and an analysis by initial rates method would be more attractive. In addition the initial rates of reaction avoids any uncertainty resulting from the change in temperature of the system due to the exothermic nature of the reaction so that again the initial rate of the reaction could be obtained at a fairly well defined temperature. We shall simply take the rate of change of conductance corrected for cell constant i.e. $\frac{d(\frac{C}{C_o})}{dt}$ as a measure of the rate of reaction with time.

Assuming that the uncatalysed reaction is given by

$$\text{Rate} = k'[\text{ligninsulphonate}]^{k}[Cr_2O_7^{=}]^{\ell}[H^+]^{m}$$

and for catalysed reaction

$$\text{Rate} = k''[\text{ligninsulphonate}]^{K}[Cr_2O_7^{=}]^{L}[H^+]^{M}[Fe^{3+}]^{N}$$

The conductance for varying initial concentrations of the reagents were measured while the initial pH's were taken at thirty seconds after mixing to pass over the 'induction' period. The initial rates were calculated by plotting for $\frac{C}{C_o}$ against time and reading for slope at

zero time. The orders of reaction obtained were:
$k = -0.41$, $\ell = -2.40$, $m = 0.17$ and $K = -4.26$,
$L = 0.45$, $M = -1.16$ and $N = 0.05$.

The orders for both reactions were non-integrals and of varying signs supporting our earlier impression of complex mechanisms. The kinetics of uncatalysed reaction appear to be different from that of catalysed one, this would be expected as the role of the catalyst is to produce a new reaction path altogether.

It is surprising that the order with respect to ferric chloride concentration is almost zero in its capacity as a catalyst. The order of catalyst concentration was also studied by an alternative application of the initial rates method. If the concentrations of lignin-sulphonate, dichromate and hydrogen ions are constant, the rate expression could be reduced to

$$\text{Rate} = z[\text{ferric chloride}]^{\ell}$$

or $$\log(R) = \log z + \ell \log[\text{ferric chloride}]$$

Using initial values, a plot of log R versus log[ferric chloride] will give a straight line of slope ℓ. Copper chloride which showed less tendency to hydrolyse in ligninsulphonate solution was also tested in comparison with ferric chloride.

Figs 25 and 26 showed that the orders for increasing additions of ferric chloride and copper chloride are not

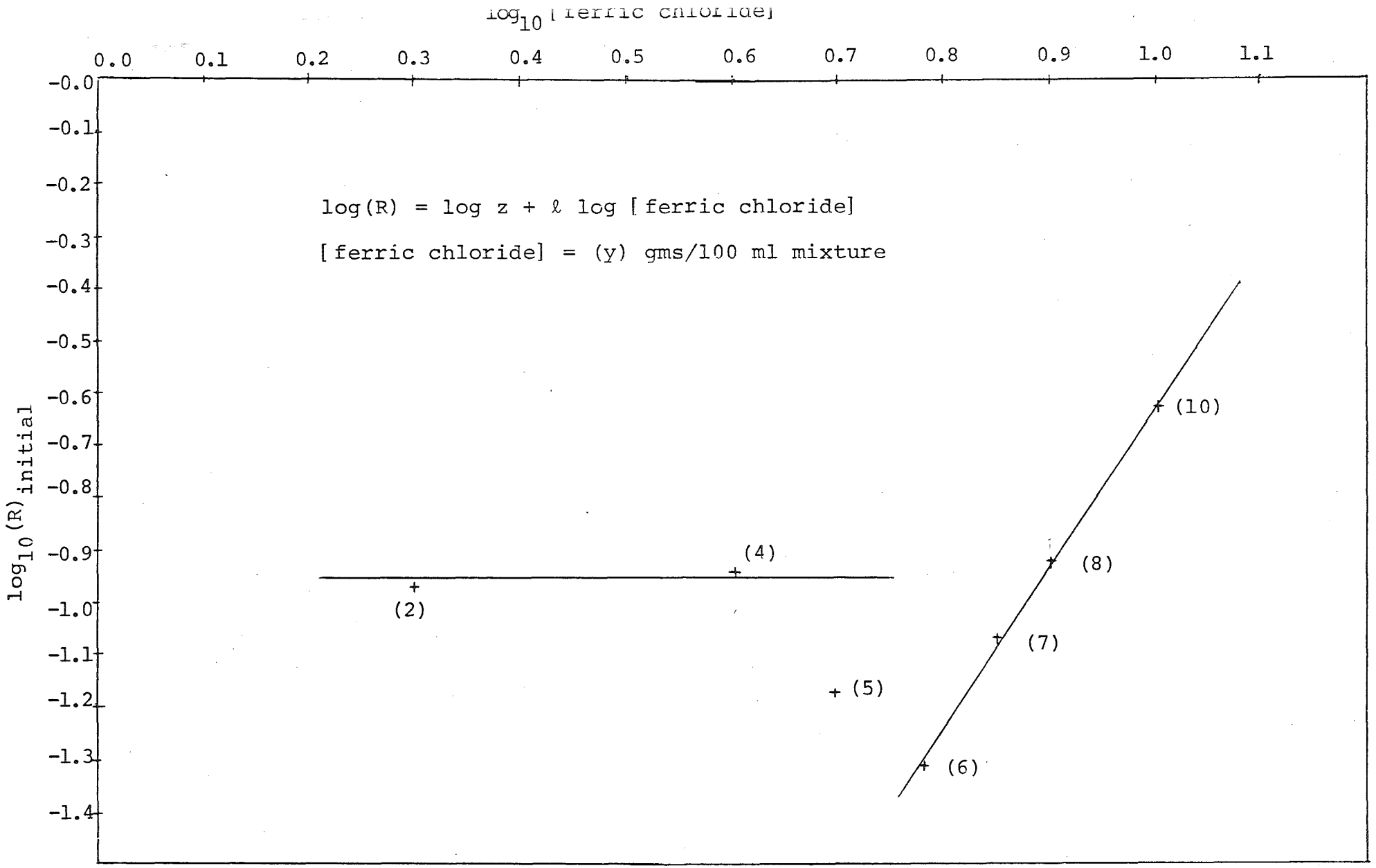


FIGURE 25: Graph of log $(R)_{initial}$ versus log [ferric chloride]

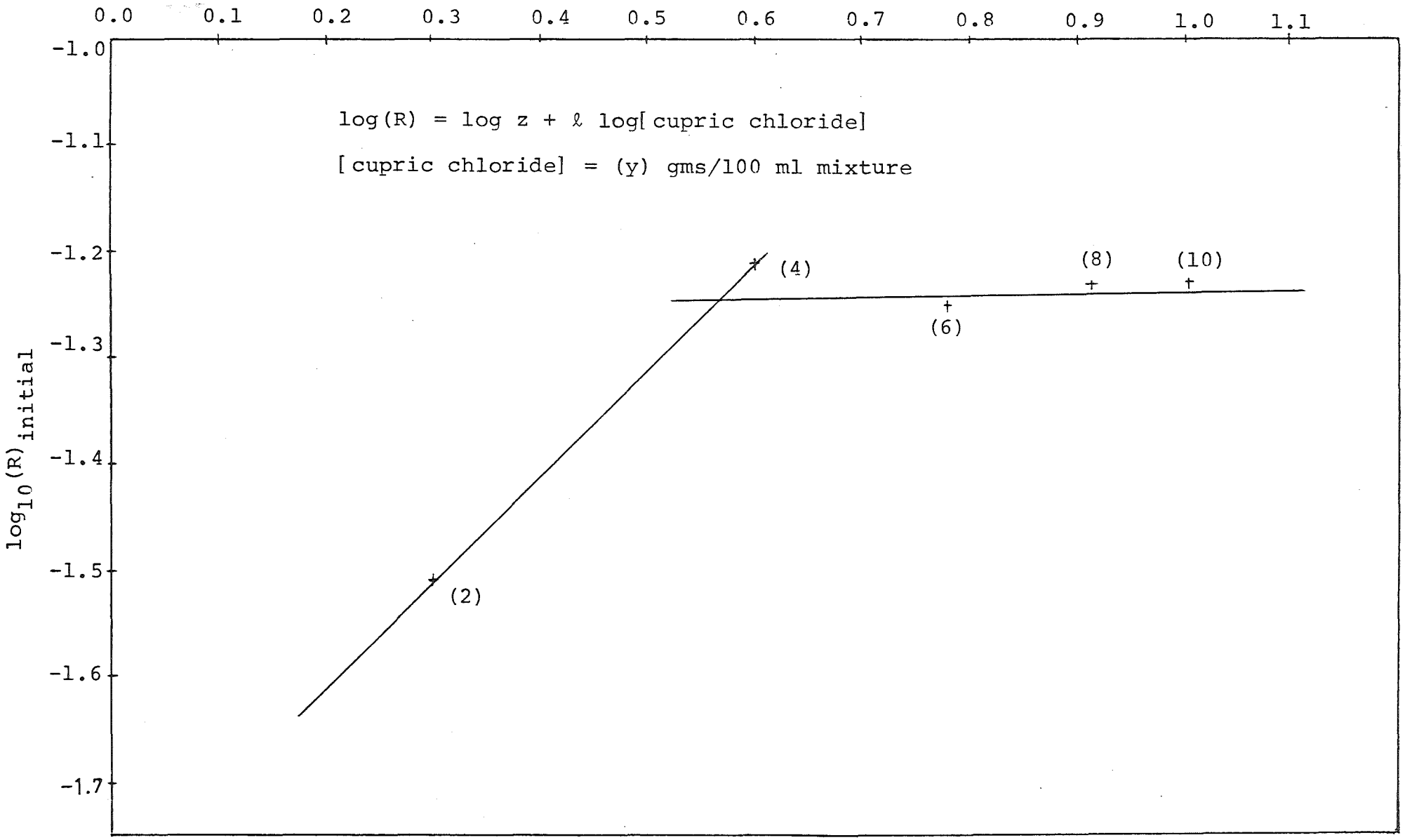


FIGURE 26: Graph of $\log(R)_{initial}$ versus log [cupric chloride]

constant. For ferric chloride, the order is zero at low concentrations and third order at larger concentrations whereas for copper chloride it is initially first order at small concentrations and then zero order at larger additions.

The validity of these results rest on the assumption that the rate of change of conductance is a measure of the rate of polymerisation and that the concentration of hydrogen ions is a constant together with all other reagents. However ferric chloride is strongly hydrolysed as too, to a smaller extent in copper chloride and this could explain for the change in order at larger concentrations. A zero order for copper chloride at large concentrations does not correspond well with the high activity of the salt over a wide range of additions observed by Akahane.

5.10 Kinetic Investigations with Viscosity Measurements - Determination of effects of hydrogen ions and to resolve its contribution from that of metal ions from additions of metal chlorides on the gelation

In order to separate the contribution to gelation time by the hydrogen ions resulting from hydrolysis from the contribution from the metal ions, the setting of gels whose initial pH were varied by addition of quantities of hydrochloric acid was measured. This may then be compared with similar mixtures catalysed by additions of metal chlorides.

Gel mixtures with a total volume of 46.6 mls were made as described in Chapter III. The amount of metal chloride added was calculated to give the same spread of hydrogen ion concentrations added as with hydrochloric acid assuming these salts hydrolysed completely in water.

The viscosity was monitered with the torsion wire viscometer and the initial pH was taken at thirty seconds after mixing. The glass electrode was conditioned as has already been described with dilute permanganic acid solution.

The setting times in table 5 were plotted against initial pH, and the following features may be observed in fig. 27.

(a) Hydrochloric acid.

The effect of initial pH is such that there is a linear fall in setting time as the pH falls from 4.8 to a minimum at about 2.5 and then rising steeply again as the initial pH falls further.

(b) Aluminium chloride.

There was a close duplication of the hydrochloric acid curve over a wide range of additions and this strongly suggests that at least in those amounts added, the 'catalytic' effect of aluminium chloride appears principally as resulting from effects of hydrogen ions released by its hydrolysis.

The curve also featured a minima as was reported by Akahane which however deviates from the hydrochloric acid

Table 5: Setting times and initial pH's of gel. mixtures for varying amounts of hydrochloric acid and metal chlorides. Temperature = 25°C.

(a) 30 mls of 50% ligninsulphonate + 6.6 mls of "50%" dichromate + X mls of conc. hydrochloric acid + (10-X) mls water.

Moles of hydrochloric acid	Setting Time (mins.)	Initial pH
0.0000	29.000	4.80
0.0104	14.500	3.70
0.0208	5.400	3.00
0.0312	3.375	2.85
0.0416	2.500	2.60
0.0520	2.950	2.45
0.0624	3.175	2.25
0.0832	2.250	2.10
0.1040	31.000	1.60

(b) 30 mls of 50% ligninsulphonate + 6.6 mls of "50%" dichromate + 10 mls water + y mls Aluminium chloride

Moles of Aluminium chloride added	Setting Time (mins.)	Initial pH
0.003465	17.35	3.92
0.007499	11.50	3.45
0.010416	8.85	3.40
0.013866	9.00	3.30
0.017335	7.00	3.11
0.020796	7.30	3.12
0.027734	6.80	3.00
0.034669	6.20	2.81

(c) 30 mls of 50% ligninsulphonate + 6.6 mls of "50%" dichromate + 10 mls water + y moles ferric chloride

Moles of ferric chloride	Setting Time (mins.)	Initial pH
0.003458	26.25	3.20
0.006942	8.25	2.85
0.010394	1.50	2.45
0.013865	<0.50	2.35
0.017332	<0.30	2.00

(d) 30 mls of 50% ligninsulphonate + 6.6 mls of "50%" dichromate + 10 mls water + y moles cupric chloride.

Moles of cupric chloride	Setting time (mins.)	Initial pH
0.005202	2.23	4.50
0.010397	0.50	4.29
0.015596	0.30	4.02
>0.015596	sets almost immediately	<4.02

(e) 30 mls of 50% ligninsulphonate + 6.6 mls of "50%" dichromate + 10 mls of water + y moles manganous chloride.

Moles of Manganous chloride	Setting Time (mins.)	Initial pH
0.002603	10.95	5.08
0.007792	5.85	4.85
0.012986	4.30	4.70
0.015592	3.90	4.51
0.018204	3.78	4.70
0.023399	3.23	4.53
0.028595	2.85	4.56

(f) 30 mls of 50% ligninsulphonate + 6.6 mls of "50%" dichromate + 10 mls water + y moles chromic chloride.

Moles of chromic chloride	Setting Time (mins.)	Initial pH
0.003460	16.60	4.20
0.003470	22.50	4.49
0.006933	11.30	3.85
0.006930	13.80	4.11
0.001039	11.45	3.70
0.013863	9.90	3.70
0.017335	8.80	3.68
0.020795	9.55	3.69

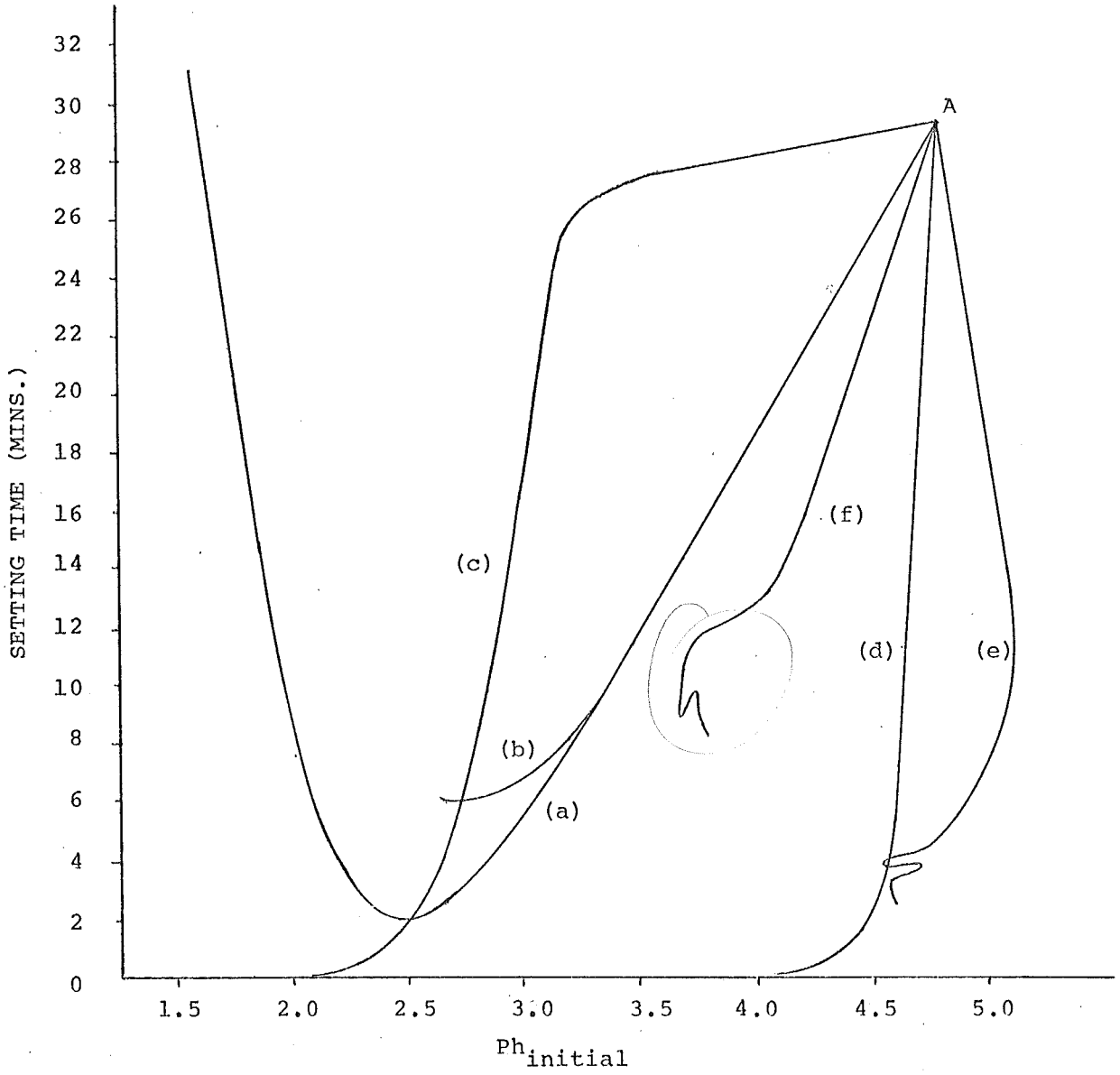


FIGURE 27: Graph of setting time versus initial ph of gel mixtures for additions of (a) hydrochloric acid, (b) aluminium chloride, (c) ferric chloride, (d) cupric chlroide, (e) manganous chloride, (f) chromic chloride to an uncatalysed mixture, A, at 25°C

curve at about this point beginning around pH 3.2. In this region the aluminium chloride system is less effective than the hydrochloric acid curve, this discrepancy can be explained as due to incomplete hydrolysis of aluminium chloride at high concentrations.

(c) Ferric chloride.

An unusual feature is seen that for quite some amounts added, the catalytic effect of the salt is in fact negative in that the material is less effective than if hydrogen ions alone have been added (i.e. for the same initial pH). This was so for initial pH's down to 2.5 and only below this did the salt begin to show positive catalytic effects. Significantly the region of negative catalysis consists of an initial plateau for small amounts and down to pH of about 3.2, then the curve starts to drop steeply and intersects the hydrogen ion curve at its minimum.

The initial plateau of inhibition of the system is probably due to the complexing of the ferric ions possibly by the lignin molecule at its active site and deactivating it from polymerisation. If this is so, the sharp decrease of curve after the plateau would indicate that the complexed ferric ion is being progressively displaced from the active site by higher hydrogen ion concentration until at pH 2.5 which corresponds to the minima of hydrogen ion curve does the effect of ferric chloride turn positive and strongly exerts over the negative effects of higher hydrogen ion concentrations.

Table 6: Setting Times and Initial pH for Additions of Hydrochloric Acid and ferric chloride at 20°C.

(a) 30 mls of 50% ligninsulphonate + 6.6 mls of "50%" dichromate + X mls con hydrochloric acid + (10-X) mls water.

Moles of hydrochloric acid	Setting Time (mins.)	Initial pH
0.0000	51.00	4.90
0.0104	15.60	3.42
0.0208	5.55	2.75
0.0416	4.45	2.25
0.0624	13.00	1.70

(b) 30 mls of 50% ligninsulphonate + 6.6 mls of "50%" dichromate + 10 mls water y moles ferric chloride.

Moles of ferric chloride	Setting Time (mins.)	Initial pH
0.0074	32.25	2.89
0.0111	21.00	2.61
0.0148	10.75	2.50
0.0185	4.25	2.35
0.0223	2.00	2.25
0.0296	0.75	2.05

(c) 30 mls of 50% ligninsulphonate + 6.6 mls of 50% dichromate + 0.0037 moles ferric chloride (point on plateau) + X mls conc. hydrochloric acid + (10-X) mls water.

Moles of hydrochloric acid	Setting Time (mins.)	Initial pH
0.0000	43.00	3.82
0.0052	24.00	2.99
0.0104	14.20	2.65
0.0260	3.05	2.50
0.0416	3.00	2.05
0.0832	29.00	1.18

To test our proposition that the catalysis by ferric chloride involved the formation of a complex and that its positive effect below pH 2.5 was due to the release of the ferric ions by hydrogen ions, a second experiment was performed in which a system corresponding to a point on the plateau was chosen and additional amounts of hydrochloric acid was added. We would expect the release of ferric ions by the acid would speed up the setting time.

The action of hydrogen ions on the ferric ion complex shown in table 6 and summarised in fig. 28 showed that additions of the acid did in fact reduce the setting time of an original point on the plateau. This acceleration could be argued as resulting from the increased hydrogen ion concentration artificially added, but it should be noted that below 2.5 the gelation was actually faster than it would have been had that pH been achieved by addition of hydrochloric acid. In this region it is evident that the accelerating effect is the combined activity of hydrochloric acid and the small amount of ferric ions added being active. Hayashi[23] has shown that the bonds of active sites with ferric ions could be cleaved with acidic cation exchanges, the hydrogen ions probably replacing the sites of displaced ferric ions.

Two reasons can be forwarded for the release of complexed ferric ion at the active sites.

(1) The mere effects of increased concentration of the hydrogen ions.

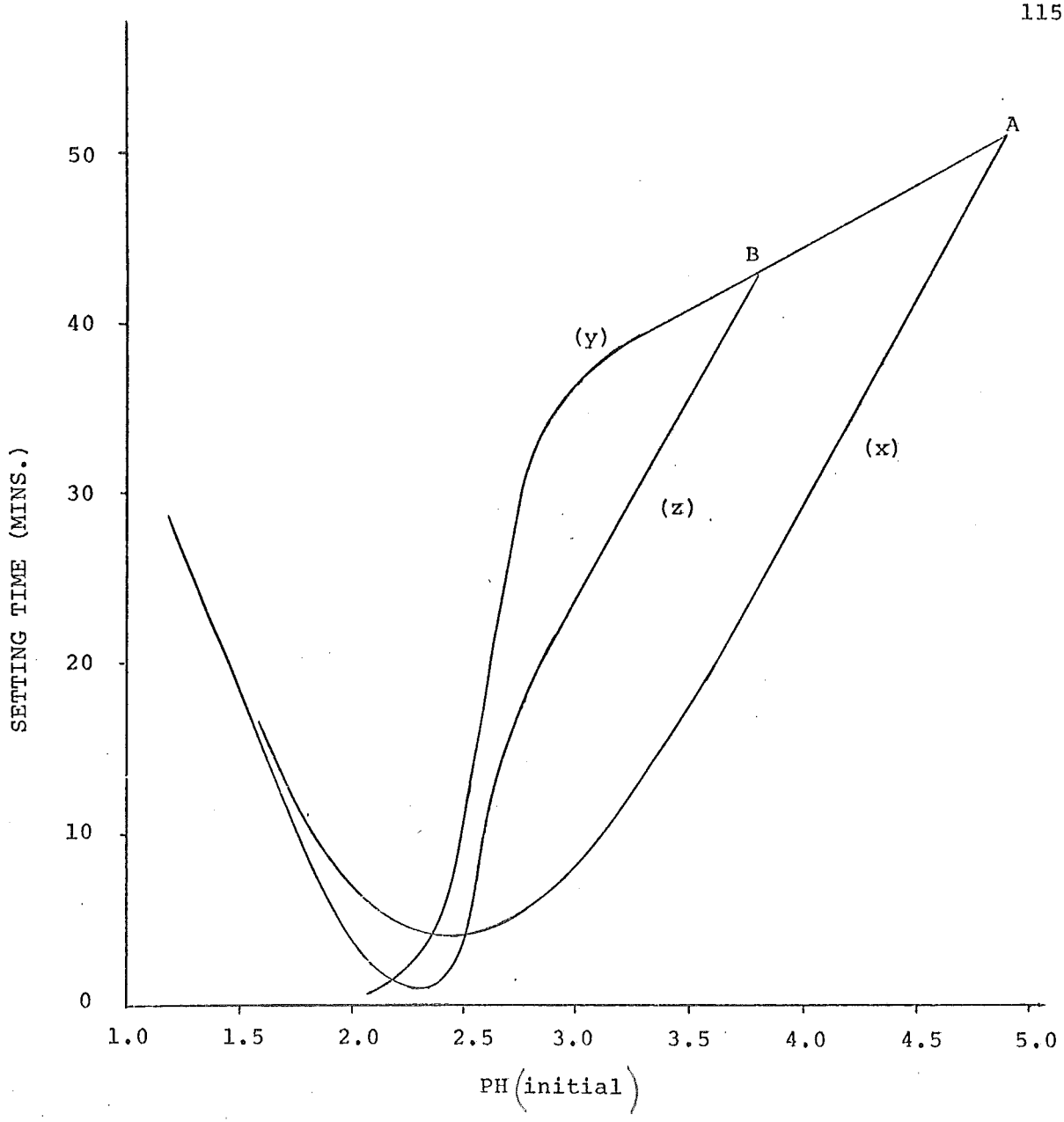


FIGURE 28: Graph of setting time versus initial ph showing effects (z) of additions of hydrochloric acid to a system, B, on the plateau of the ferric chloride curve (y); (x) is the curve for addition of hydrochloric acid to uncatalysed system, A, at 20°C.

(2) The stability of the ferric ion in the aqueous phase is increased by competitive complexing with the chloride ions from the hydrochloric acid additions resulting in a transfer of ferric ions from the active sites to form the more stable chloride complex $(FeCl_6)^{3-}$. Hayashi[17] demonstrated that the most obvious active sites in the lignin molecule are the pendent catechol groups and conductometric titration gave the log of the stability constant[29] of its chelation with ferric ion as 5.30 while that of the chloride complex with iron (III) is typically very much less,[32] the actual value of the latter is dependent on the medium employed. These figures indicate that the complexing action by chloride ions is a far less likely mechanism than the concentration effects of hydrogen ions.

The ferric chloride curve was repeated at two different temperatures 25° and 20°C, and at the second temperature, the plateau region extended over a wider range of pH from 4.9 to 2.7 than that at the higher temperature from 4.8 to 3.2. This is further evidence of the complex formation with ferric ions as in general, the lower the temperature the more stable the complex.

(d) Cupric chloride.

Fig. 27 shows that copper chloride is much less hydrolysed in ligninsulphonate solutions and the acceleration

in this case is mainly that of the metal ion.

The salt appeared to have the greatest catalytic effect among all the metal chlorides added, this is clearly seen in a plot of setting time against moles of chlorides added to 46.6 mls mixtures, fig. 29. Even for reasonably small amounts e.g. 0.004 moles, the setting time was dramatically reduced from 29 minutes to 4 minutes compared to 8 minutes for manganese, 17 minutes for aluminium chloride, 21 minutes for chromic chloride, 23.5 minutes for hydrochloric acid and 25 minutes for ferric chloride. For large quantities e.g. 0.012 moles, the gelation with cupric chloride was almost instantaneous and only ferric chloride was comparable in performace. This comparison was similar to that somewhat observed by Akahane. The order of acceleration of chlorides for moderate additions (0.005 - 0.007 moles) is $Cu^{2+} \gg Mn^{2+} > Fe^{3+} > H^{+}$, Al^{3+}, Cr^{3+} and for large additions ($\gg$ 0.008 moles), $Cu^{2+} > Fe^{3+} \gg Mn^{2+} > H^{+} > Al^{3+} > Cr^{3+}$.

The catalytic efficiency of copper (II) is remarkable among all others and a number of reasons for its exceptional performance could be deduced. Hayashi[23] showed that the darkening of colour of copper(II) with tiron as a model compound was much less than that of iron(III) and in fact, unlike iron(III), was not visible at all with ligninsulphonate solution. This is supported by a stability constant of chelation with ligninsulphonate of only 2.50 compared to 5.30 for iron(III). Copper(II) clearly demonstrated an optimum stability in its complexing with ligninsulphonate which is a prime

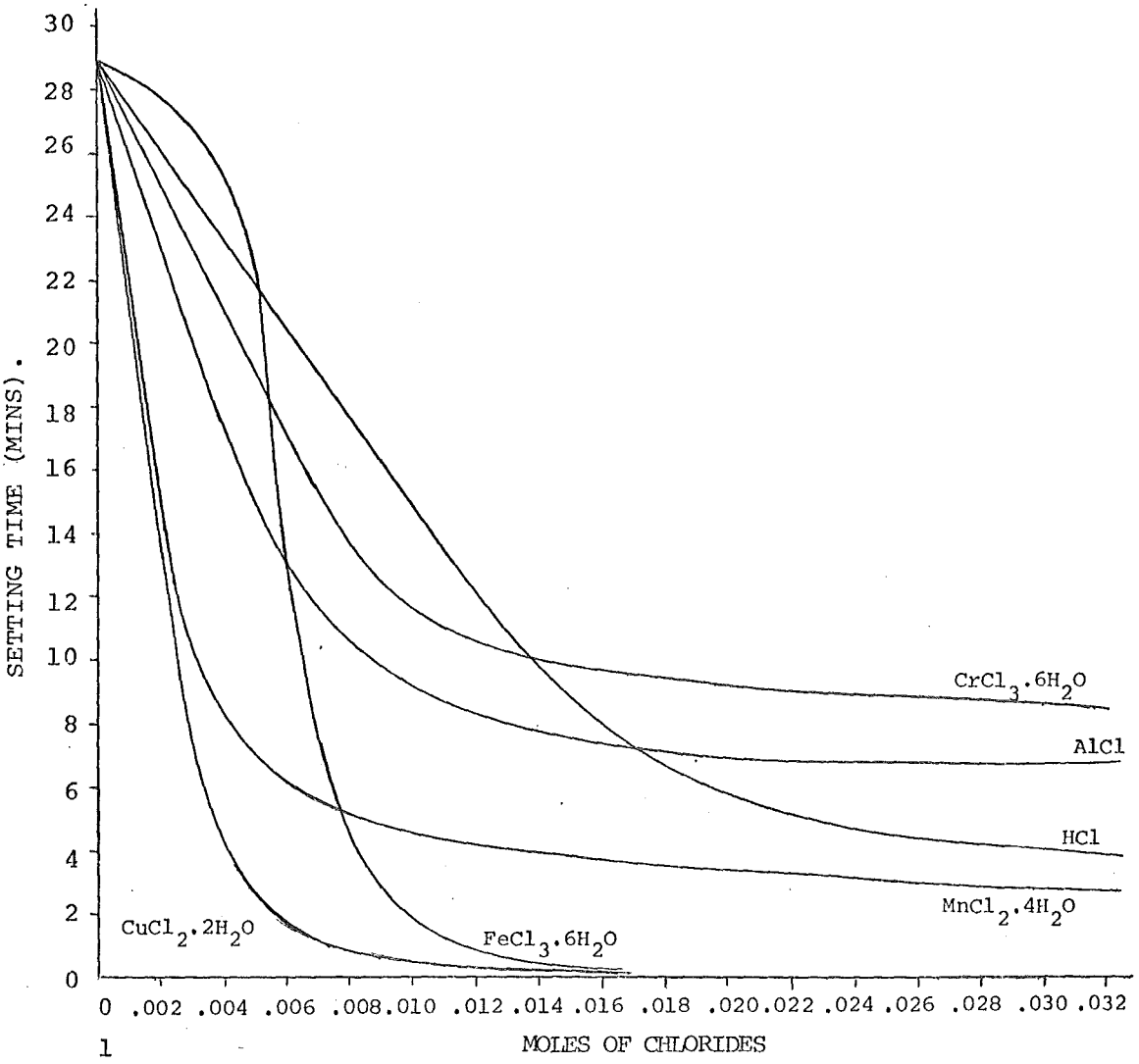


FIGURE 29: Graph of setting time versus amounts of hydrochloric acid and metal chlorides added to a 50% ligninsulphonate gel mixture.

prerequisition for an active catalyst. In general, although copper(I) and (II) have strong tendencies to form coordination complexes[33] they are much less capable of doing so in chelation with the pendent catechol groups because with a coordination number of only 2, the same catechol group would have to connect at opposite sides of the metal atom. The complexing of copper(II) would therefore be a weaker one than iron(III) and would not be sufficiently strong to block the active sites. Further, copper(I) complexes are generally less stable than those of copper(II) and an unstable copper(I) complex with the oxidised active site could provide the driving force for the slow breakdown of the complex and speeding up the catalytic cycle. Together with a low reduction potential, copper (II) appears to have all the ingredients of a good catalyst and thus explains for its high activity.

(2) Manganous chloride

The pH of mixtures containing manganous chloride additions showed that the catalysed mixtures are more basic than a non-catalysed one, fig. 27. Like ferric, aluminium and cupric hydroxides, manganous hydroxide is a weak base and its chloride salt should hydrolyse with release of hydrogen ions. It is probable that the manganous ion is oxidised by dichromate to Mn(III) or higher with the consequent loss of H^+.

In the absence of possible significant hydrogen ion "activity", the acceleration of gelation would be entirely

that of the manganous ion and is seen to be next to copper(II) and iron(III) in order of activity overall, fig. 32. The factor controlling the activity of manganous ion is different from that for ferric ion.

Assume that the oxidation-reduction cycle of the catalyst involves higher oxidation states of manganese. The manganese(II) is known to have a weak tendency to form complexes and while the higher oxidation states of manganese e.g. Mn(III) and Mn(IV) are relatively unstable they are considerably stabilised by coordination[33]. Thus like copper, manganese is expected to form favourable concentrations of complexes and to exert significant catalytic activity but would be considerably reduced by the inhibitively large reduction potentials generally showed by manganese ions.

(f) Chromium chloride.

The chromic chloride does undergo some degree of hydrolysis and releasing hydrogen ions from fig. 27 while fig. 29 shows that the catalytic effect of chromic chloride is small among all the additives. This seems to suggest that the acceleration by chromic chloride is solely that of hydrogen ions and that the chromium (III) ion itself is basically inactive.

Chromium(III) is known to form stable complexes with many ligands and its stability constant with ligninsulphonate complexation of 3.40 is only next to that of ion(III) 5.30 in magnitude. However like all other metal chlorides investigated, chromic chloride does not produce a plateau.

region of negative catalysis as with ferric chloride so that its stability with ligninsulphonate complexation is not sufficient justification alone to explain for the apparent inactivity of chromium(III) ions. The dominating factor in this case would be the well known property of chromium(III) to form complexes which are also kinetically inert[30,33] especially with chelating agents. Ligand displacement reactions of the chromic complexes are typically found to have half-times in the range of several hours.

5.11 A System of Data Analysis for Subtraction of Hydrogen Ion Contribution from Metal Chloride Additions

Fig. 27 simply shows whether the metal ions have a positive, negative or zero catalysis. In order to get a clearer indication of the effects of a metal ion on the gelation, it is necessary to derive some system of data analysis whereby the contribution from hydrogen ions can be subtracted. This is done by assuming that the gelation occurs by a number of parallel routes involving simultaneous activity of the hydrogen ions and the metal ions and the setting time is the sum of their reciprocal contributions which include:

(1) The fundamental zero-catalyst setting time.

(2) The setting time contribution due to the metal ion catalyst.

(3) The setting time contribution from the hydrogen ions released from hydrolysis of the chloride salts.

The reciprocal setting time contribution by the metal ion can be calculated by subtraction of reciprocal setting time contribution of "equivalent hydrogen ions of hydrolysis" from the reciprocal setting time of the gel.

$$\text{i.e.} \quad \frac{1}{t_{M^{n+}}} = \frac{1}{t_{gel}} - \frac{1}{t_{H^+}\ \text{equivalent}}$$

$$= \frac{1}{t_{gel}} \quad \frac{1}{t_{\text{initial pH of mixture}}} \ .$$

To do this, a calibration graph between reciprocal setting times and initial pH was first obtained for an uncatalysed gel, the initial pH of which was varied by additions of hydrochloric acid. Using table 5 and the calibration graph, the reciprocal setting time contributions by metal ions were calculated and plotted against the amount of metal chloride added. For comparison, the reciprocal of uncorrected reciprocal setting times were also plotted against moles of chloride salts taken, figs 30 and 31.

Inspection of figs. 30 and 31 show that the linearity of the curves are generally improved after correction for hydrogen ion contribution, especially for copper(II), iron(III), manganese(II) and aluminium(III). This indicated that the correction adopted was a satisfactory one.

An analysis of fig. 31 generally confirms the findings deduced from fig. 27 in the last section.

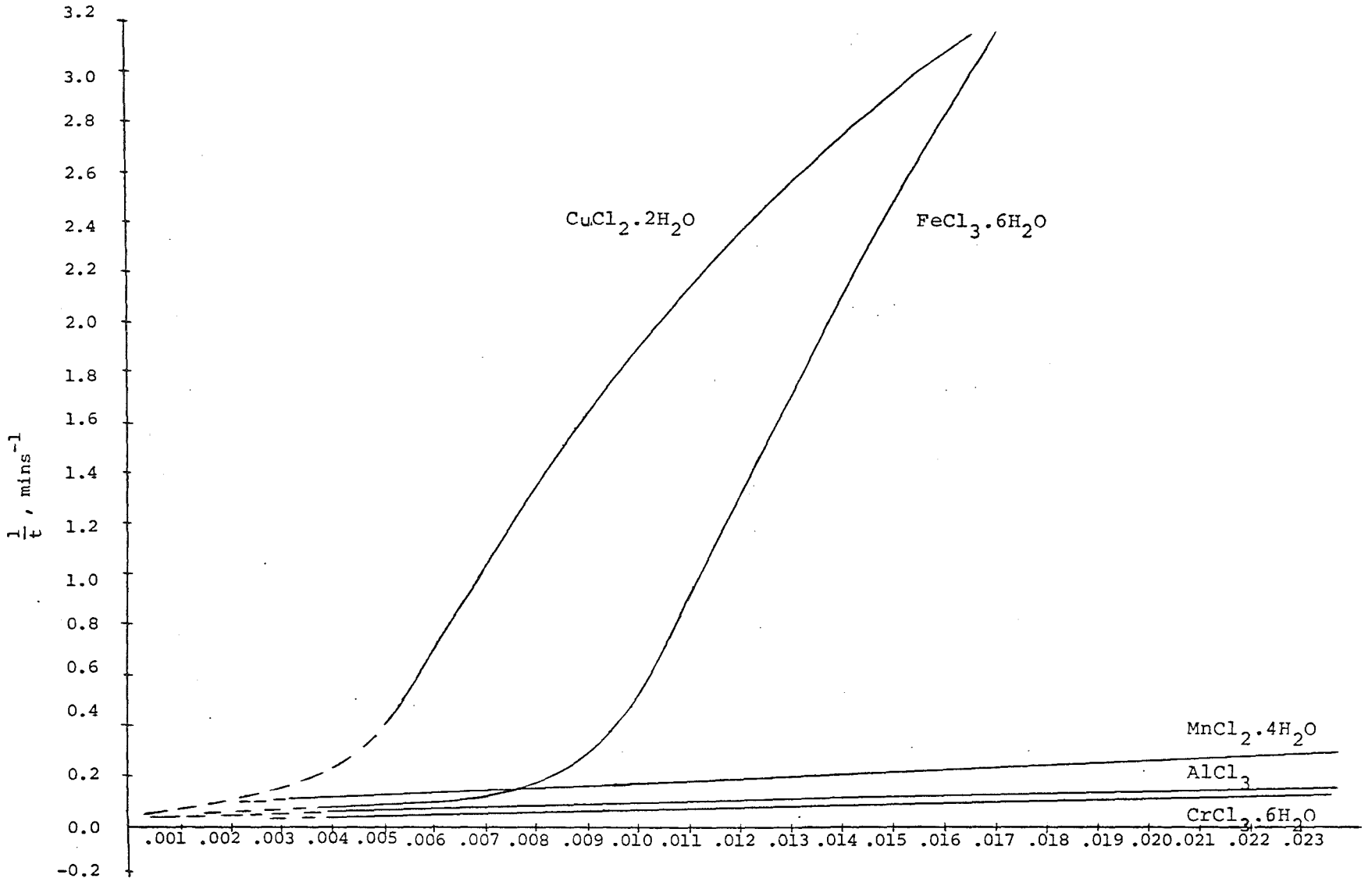


FIGURE 30: Graph of reciprocal setting time versus moles of chlorides added to a 50% ligninsulphonate gel mixture.

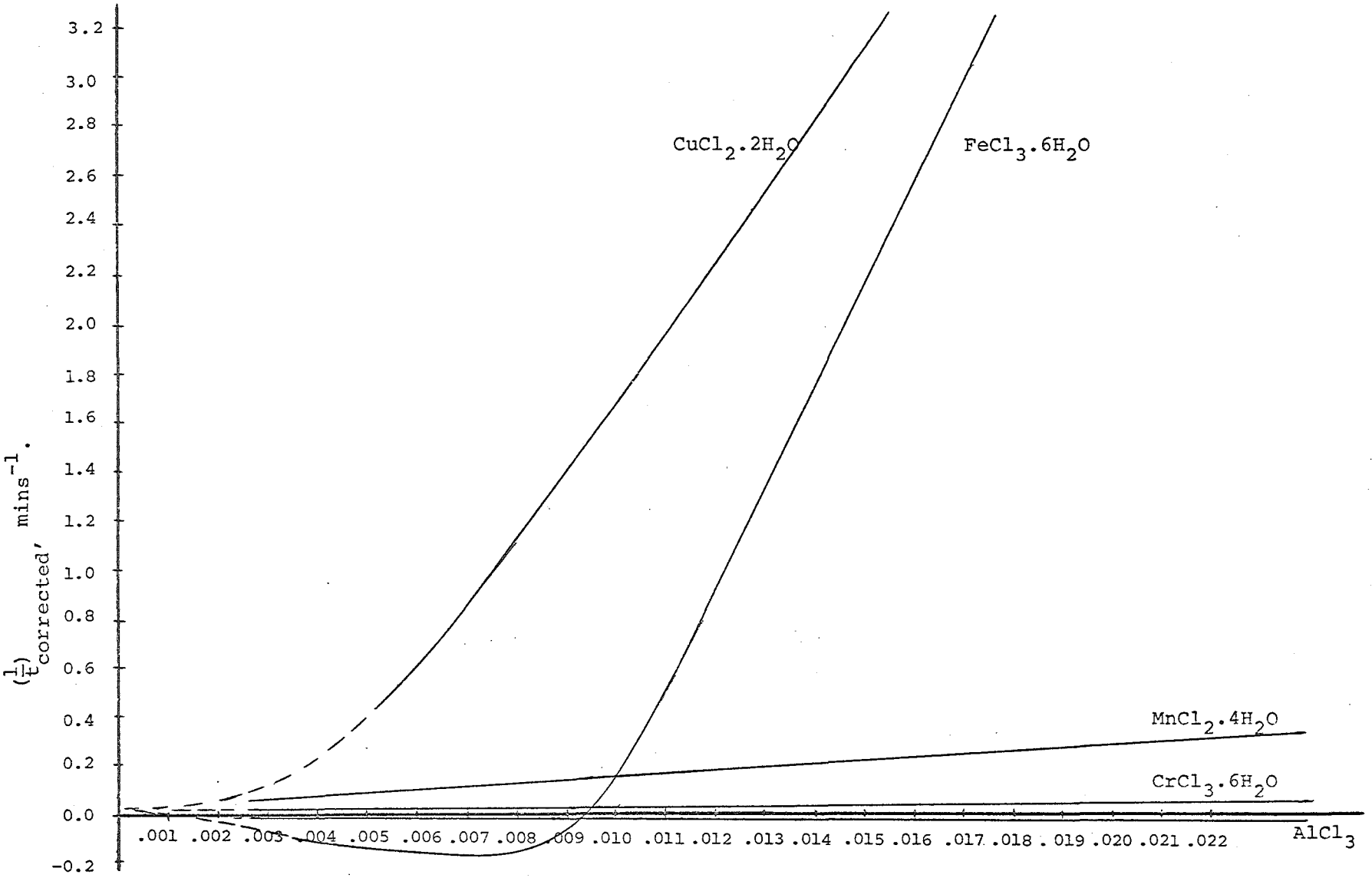


FIGURE 31: Graph of corrected reciprocal setting time versus moles of chloride added to a 50% ligninsulphonate gel mixture.

(a) Ferric chloride.

For the additions of ferric chloride investigated, the curve consists of an initial "negative" section for low concentrations of the salt which correspond to the plateau region of negative catalytic activity in fig 27, and thenfollowed by a steep rise which is reasonably linear. As much as reciprocal setting time is a measure of the rate of reaction, it would appear that iron(III) is catalytically first order for additions > 0.01 moles in 46.6 ml. mixture.

The curve obtained is in agreement with our earlier hypothesis that initial additions of iron(III) inhibit polymerisation by strong complexation and blocking the active sites and only at larger additions or lower initial pH is the release of complexed iron induced and the iron(III) ion be permitted freely display an electron-transfer role. It is certain that the strong complexation of iron with ligninsulphonate is formed. The large stability constant of 5.30[29] measured and a big shift detected in the visible spectrum of the complexed polymer (refer next section) give conclusive evidence to this.

(b) Cupric chloride.

The curve is reasonably linear indicating that the setting time is essentially first order with respect to the amounts of copper added. It is noticed however, that the straight line does not pass through the point corresponding to zero-catalyst reaction ($\frac{1}{t_o}$ = 0.034 min^{-1}) and possess a

region of non-linearity at low additions suggesting a possible inhibitive complex formation but which is much less severe than that of iron(III) as the region of zero order is far less extensive. Taking the slopes of the curves as proportional to the catalytic activity of the metal ions, it is seen that for concentrations past the plateau region, copper(II) is less effective than iron(III) but due to the extensive initial region of negative catalysis for iron (III), the absolute activity of copper(II) is greater at any concentration.

(c) Manganous chloride.

The manganese(II) curve is generally linear and is slightly sloping indicating that the metal ion has a positive catalytic contribution and the reaction is approximately first order for all manganese concentrations. The activity of manganese(II) is clearly smaller in comparison to that of copper(II) and iron(III).

On closer examination, the role of manganous chloride as an electron-transfer catalyst is complicated as the manganese(II) ion has little or no reducing properties[34]. With a reduction potential of 1.51 volts Mn(II) oxidises with considerable difficulty to Mn(III), which at the same time is so unstable that it has virtually no aqueous solution chemistry unless stabilised by complexation. The actual species of manganese involved in the catalytic cycle is therefore uncertain.

Due to the murkiness of the polymerising mixture and a host of complex reactions taking place at once, it

would be difficult to identify for the active species involved. It might be profitable especially in this case to employ model systems to identify for the particular working species constituting the oxidation-reduction couple of catalyst.

(d) Aluminium chloride.

Both curves gave essentially horizontal straight lines. Their setting times are independent of their concentrations which mean that the metal ions are catalytically inactive.

From a knowledge of the aqueous chemistry of aluminium chloride and the above data, we can reject any hypothesis that aluminium(III) has any catalytic activity. This leaves without any doubt that the apparent activity of the chloride salt is solely due to the hydrogen ion concentration released on hydrolysis.

The horizontal slope of the chromium(III) curve also indicates that the metal ion has no other contribution except that due to hydrogen ions from the salt. In this case the situation is slightly complicated by the fact that chromium(III) ions are also being produced in solution from the reduction of the dichromate ion and the apparent absence of activity could probably be due to the presence of sufficiently large quantities of the chromium(III) produced from the polymerisation which swamps the contribution added artificially. From the stoichiometric relation determined in Chapter III, the amount of chromium (III)

produced from a 46.6 ml mixture after 24 hours reaction would be estimated to be about 0.018 moles while the amounts artificially added ranged from 0.003 moles to 0.021 moles.

While the "swamping" effect appeared to be viable to some extent in fig. 31 alone, fig. 29 on the other hand clearly showed that the catalytic activity per mole of chromic chloride is only similar to that of aluminium chloride and hydrochloric acid. The large amounts of chromium(III) ions introduced and produced in the mixture is far less effective than that of the other two additives and would undoubtedly indicate that the chromium(III) is rather inactive.

5.12 Polarographic and spectrometric evidences for complex formation between heavy metal ions and calcium ligninsulphonate.

A. Polarographic evidence

Polarographic measurements were conducted to detect the presence of complexes between heavy metal ions and ligninsulphonate employing both the dropping mercury electrode and the rotating platinum electrode.

Hayashi et al[35] investigated the chelating action of ligninsulphonate with iron(III) and cobalt(III) by observing the shift of the half wave potential of the metal ion and the increase in height of the reduction wave as ligninsulphonate was increased and concluded that the interaction between the polymer and heavy metal

ions is one of chelation e.g. the reduction wave of 2.5×10^{-2} moles ferric chloride in 0.3N acetate buffered at pH 5.0 was shifted progressively to negative potential to around - 0.15 volts.

In the following experiments to obtain similar polarographic evidence, investigation on all five metal ions in Al^{3+}, Fe^{3+}, Cu^{2+}, Mn^{2+} and Cr^{3+} were performed. As Hayashi[23] reported that it took a considerably long time to complete the complex formation of the ferric ion with ligninsulphonate (requiring at least three days at room temperature), a freshly made iron(III) complex from that of a complex aged for three weeks was also examined.

Cathodic polarograms at a dropping mercury electrode were observed using a potassium chloride electrolyte cell containing calcium ligninsulphonate with additions of metal chloride solutions. The solutions for all experiments were purged with nitrogen. The essential results are presented below.

Table 7: Typical cathodic half wave potentials with potassium chloride as supporting electrolyte.

Compound/Mixture	$E_{\frac{1}{2}}$ volts
Ligninsulphonate	-0.940
Al^{3+}-ligninsulphonate	-0.945
$(Fe^{3+}\text{-ligninsulphonate})_{fresh}$	-0.905
$(Fe^{3+}\text{-ligninsulphonate})_{3\ weeks}$	-0.800
Cu^{2+}-ligninsulphonate	-0.950

The results were not particularly reproducable and except for the aged iron complex all other half wave potentials do not give any distinct shift from that of ligninsulphonate. This was probably due to the precipitation of the metal hydroxides so that complexation never occured. Some precipitation was in fact observed. To ensure complexation, a dilute solution of ligninsulphonate (1.0%) as supporting electrolyte was used and amounts of metal chloride solutions added until a new wave was obtained.

Table 8: Typical cathodic half wave potentials with dilute ligninsulphonate as supporting electrolyte.

Compound/Complex	$E_{\frac{1}{2}}$ volts
Ligninsulphonate	-0.871
$(Fe^{3+}\text{-ligninsulphonate})_{fresh}$	-0.910
$(Fe^{3+}\text{-ligninsulphonate})_{3\ weeks}$	-0.840

No improvement in reproducability was found with the new cell solutions. Any significant indication of complexing is for iron in the mixture aged three weeks which supported Hayashi's result.

The most plausible reason why ligninsulphonate does not seem to lend itself to polarographic study is that it has been found to be polarographic inactive.[36] In a series of papers on the polarography of lignin materials and model compounds, Kanda and co-workers[6] showed that

it is the -C-CO-aryl grouping that is the most probable contributing structure responsible for the cathodic half wave potentials. It would therefore not be surprising that no genuine metal ion-ligninsulphonate complex half waves could be expected since the complexing agent in the ligninsulphonate molecule was never shown to involve the carbonyl group but some other like the catechol group.

A different experimental approach was next adopted. Since the active sites of ligninsulphonates would be negatively charged groups, the molecule would be expected to yield anodic half waves characteristic of the active sites. Addition of heavy metal ions would shift this potential on complexation and the relative magnitude of shift would give an actual indication of the relative strength of complexation of active sites with the various metal ions. And as the polymerisation is an oxidative process, the anodic half wave potentials would be more directly relevant to its kinetics than the cathodic ones.

The anodic waves were obtained using a rotating platinum disc as the working electrode in conjunction with a stainless steel cathode. The applied potential was measured between the rotating platinum anode and a standard calomel electrode and both current carrying electrodes were carefully cleaned in permanganic acid solutions. 1.0% ligninsulphonate solution as supporting electrolyte was used as before.

Table 9: Typical anodic half-wave potentials with dilute ligninsulphonate as supporting electrolyte

Compound/Complex	Anodic halfwave potentials
Ligninsulphonate	0.743
$(Fe^{3+}$-ligninsulphonate$)_{fresh}$	0.890
$(Fe^{3+}$-ligninsulphonate$)_{3\ weeks}$	0.377 and 0.820 (two peaks)
Cu^{2+}-ligninsulphonate	0.797
Mn^{2+}-ligninsulphonate	0.880
Cr^{3+}-ligninsulphonate	0.770
$Cr_2O_7^{=}$-ligninsulphonate	0.820

Generally, the anodic half wave potentials of the complexed active sites are slightly higher though not much higher than that of the ligninsulphonate and it is doubtful if they differ sufficiently to indicate any meaningful trend to warrant a conclusion. However this is surprising as the role of a catalyst is not expected to raise the potential for oxidation at the active site but on the other hand it may well reflect the increased activation energy of the catalytic polymerisation of ligninsulphonate qualitatively observed in our measurement of setting times at two temperatures (refer next section). Also once again, the iron(III) complex is peculiar in that an aged mixture gave two waves compared to one for a fresh mixture and this could be regarded as evidence for complex formation.

B. Spectrometric evidence for complex formation of of ligninsulphonate with heavy metal ions.

When ferric chloride was added to a dilute solution of ligninsulphonate a distinct dark colouration was strongly observed as is characteristic of complex formation of organic ligands with heavy metal ions.[23] This was not discernable with the other metal ions of Al^{3+}, Cu^{2+}, Mn^{2+} and Cr^{3+}, the results of previous sections suggested that their complexations are much weaker and any colour development occuring would easily be masked by the light brown colouration of the ligninsulphonate itself anyway.

Ligninsulphonates have been studied spectrometrically[37] but mainly using substitute model compounds, hence the evidences for the ligninsulphonate complex has so far been indirect in nature. For example, Hayashi[23] studied the ultraviolet and visible absorptions of tiron as a model compound and found that iron(III) complexation shifted the ultraviolet peaks downfield while the visible absorptions were much intensified. With copper(III) ions, a similar trend was observed but the colouring effect was much less indicating a weaker complex formation.

In this work, ultraviolet, visible and infra-red spectrograms were recorded directly for solutions of ligninsulphonate with iron(III) and copper(II) ions.

(a) Spectrometric evidence for ligninsulphonate -Fe^{3+} complex.

It was found that the ultraviolet region is not an attractive region to investigate for formation of lignin-sulphonate complex species because the polymer strongly absorbs in this region and the concentration of complex formed from a dilute solution of ligninsulphonate is too weak to be sensed spectrometrically even though the darkening of colour developed is strongly visible.

In the visible region, ligninsulphonate absorbs less intensely and stronger solutions could be employed to generate larger concentrations of the complex.

A comparison of the absorption peaks, table 10, of the reagents from that of mixtures of similar effective concentrations showed that the complexation of iron caused a considerable shift of the ligninsulphonate bands in the direction of increasing wave-length. A large absorption downfield into the visible region would result in the darkening of colour and the distinct dark greenish tinge of the complex observed in the strong concentration mixture. No new peaks were seen.

(b) Spectrometric evidence for ligninsulphonate-Cu^{2+} complex

A stock solution of cupric chloride (0.0293 M/ℓ) showed no peaks in the visible region but the beginning of a band climbing into the infra-red region while the spectrum of a mixture of ligninsulphonate and cupric chloride stock solutions gave two absorption peaks at 378 and 514.5 nm.

Table 10: Visible absorption of ligninsulphonate, ferric chloride and complex.

Concentration of solutions	stock	$\frac{\text{stock}}{2}$	$\frac{\text{stock}}{10}$	$\frac{\text{stock}}{20}$
Ligninsulphonate peaks(nm)	392.0	374.0	U.V. region	U.V. region
Ferric chloride peaks(nm)	387.0	373.0	352.0	U.V. region

Concentration of ligninsulphonate plus ferric chloride	stock + stock	$\frac{\text{stock}}{5}$ + $\frac{\text{stock}}{5}$	$\frac{\text{stock}}{10}$ + $\frac{\text{stock}}{10}$
Ligninsulphonate-Fe^{3+} complex	large absorption peak at >> 374.0	372.5	352.0

Comparing with the ligninsulphonate peaks in table 10, the complexation with cupric ions is seen to cause a small shift in increase of wave-length of the ligninsulphonate peak from 374 to 378 nm. Such a small shift agrees well with the observed absence of a distinct darkening of colour in the mixture. This would also indicate that the interaction between the ligninsulphonate molecule and the cupric ion would be small and lend support to our earlier conclusion of a much weaker complex with copper (II) than with iron(III).

A new peak at 514.5 nm appeared to be formed giving further evidence of a complex formation. This new peak was however not well formed but appears as a "shoulder". A stronger mixture than that investigated would be expected to develope the new peak more distinctly if it is indeed real.

5.13 Some observations of potential kinetic importance

Several observations were also made in the process of physical and kinetic studies on the gelation.

(a) In catalysed mixtures, heat is often evolved and it could be attributed to arise from two different sources. From additions of large amounts of copper chloride, some amount of heat was evolved indicating that the polymerisation is itself slightly exothermic. At the same time general oxidative-degradative reactions of the ligninsulphonate macromolecule also occurred, this was indicated from additions of hydrochloric acid. For similar setting

times as with the copper chloride additions, the acidified gels evolved much larger amounts of heat and yielding markedly inferior gels with evolution of effervescence indicating degradation of the polymer was occurring which was strongly exothermic. When the initial pH was brought down below 2.5, the mixture turned greyish-black instantly instead of the usual greenish-black complexation and the mixture took progressively longer to gel. This shows that the hydrolysis is more strongly promoted by high hydrogen ion concentrations. Oxidation of the gel is also known to yield products like vanillin which could be smelled strongly in all the gels[6].

The quantities of heat evolved in additions of various metal chlorides are qualitatively tabulated in appendix C.

Copper chloride, chromic chloride and ferric chloride in small quantities released only small concentrations of hydrogen ions from hydrolysis. The slight heat evolved with these salts is mainly from the accelerated polymerisation realised from the catalytic activity of Cu(II) ion or the hydrogen ion effect in the case of the kinetically inert Cr(III) ion and the Fe(III) ion which is a retarder in these concentrations. At larger additions, the contribution from the general oxidations increases proportionally and moderate amounts of heat are observed with high concentrations of salt.

Gelations with manganous chloride gave no perceptible evolution of heat as the salt does not appear to release

hydrogen ions in the gelling mixture, it is also only slightly catalytic.

Aluminium chloride is distinctly odd because, in spite of the hydrogen ions released in large quantities, the mixture appears to remain cold during gelation with little sign of deterioration of the gel. Maybe the many sites of oxidation, presumably negatively charged, are coordinated to the highly charged non-functional aluminium(III) ions and blocking the process of hydrolysis, but this would bear further investigation probably through calorimetry.

(b) Discon was analysed in Chapter III to contain small amounts of heavy metal ions in iron, copper and manganese but their quantities were never greater than 1×10^{-5} moles in an equivalent 30 mls of 50% lignin-sulphonate solution taken for kinetic studies. From fig. 30, initial amounts of these ions gave zero order reaction in their concentrations and we could therefore safely assume that the traces of these ions in the commercial ligninsulphonate are inactive kinetically and do not play any significant role both in uncatalysed and catalysed reactions.

(c) The gelation times of catalysed mixtures with metal chloride additions were found to be very sensitive to changes in room temperature while those with hydro-chloric acid additions were far less sensitive. This

would suggest that the activation energy of the catalysed process was in fact higher than the uncatalysed reaction involving only hydrogen ions and this was supported by the polarographic anodic half wave potentials in the last section. On reflection this seems strange as normally the role of a catalyst is to provide an easier reaction involving both a lower free energy of activation and a more stabilised transition state.

The rate constant of a reaction is usually expressed as the product of a constant which is the Arrhenius factor of the negative activation energy over RT i.e. $k = Ae^{-\frac{Aa}{RT}}$. If the above observation is true then an increase in activation energy together with an increase in rate would necessarily require an increase in the frequency factor A. This seems to point to the conclusion that the principle contribution of the metal ion catalyst is to increase the frequency of the reaction i.e. the increase in the frequency factor must more than compensate for the exponential factor and that the catalysed mechanism would be a different one from the uncatalysed reaction. This effect of the metal ion catalyst is unusual though not unknown and is an area which could be subjected to further investigation though it is difficult to make precise measurements of the temperature because of the heat evolved during the course of the gelation.

(d) In taking pH measurements for the reaction mixture in table 5, there was always experienced a "blind" period for at least the first ten seconds after completion of mixing,

examine Fig. 22. In taking a while for either the reaction to get started or for an ionic equilibrium to be established between the mixture and electrode, the gelation appears to be diffusion controlled at least to some extent. This would be reasonable as ligninsulphonate is a polyelectrolyte giant molecule[20] and in order to crosslink intermolecularly the active sites of ligninsulphonate must diffuse against the repelling force of negative charges.

This contemplation was supported by the behaviour of the pH curves of gelation in which the pH increases in an oscillatory manner. Similar conductance curves were sometimes obtained but which could not be reproduced at will, all of which points to an oscillation reaction brought about by the low mobility of polymer molecules and the viscous state of the mixture restricting the rate of chemical interaction.

(e) From the measurement of viscosity of ideal gel mixtures in chapter IV, a number of preculiarities were observed in the behaviour of the gelation times.

An examination of fig. 18 showed that for a given amount of ferric chloride added, the gelling time as a function of ligninsulphonate concentration always revealed a maxima somewhere along the curves. The maxima is greatest for lower ferric chloride additions and for ligninsulphonate concentrations of around 20% - 30%. These maxima could be seen to fall neatly along a curve (broken line traced in figure 18).

In general, mixtures containing 4 gms. ferric chloride per 100 ml mixture gave the shortest gelling times for varying ligninsulphonate concentrations.

The effect of increasing amounts of ferric chloride at high concentration gels e.g. 50% ligninsulphonate solutions is observed to shorten the gelation times progressively while the reverse trend is true for dilute gels e.g. < 5% ligninsulphonate solutions.

The rheological studies of uncatalysed gelation by Hayashi[13] indicated that the concentration of ligninsulphonate is very critical for gelation. For crosslinking to occur, the minimum concentration of ligninsulphonate required is 11.6%. In contrast, mixtures catalysed by ferric chloride was found to gel successfully at concentrations well below 5% ligninsulphonate solutions. This could be attributed to the oxidative polymerisation process which probably has the capacity to produce crosslinking even at low concentrations in the presence of electron-transfer catalysts. Gelation of dilute solutions in this manner should not be impossible as few intermolecular crosslinks are sufficient for branched macromolecules to gel e.g. rubber hydrocarbon gels with just one crosslink per hundreds of isoprene units[21].

(f) When large quantities of ferric chloride were used e.g. 10 gms per 100 mls mixture, conductance measurements showed that the resistance of the gel gave a sharp rise in resistance (refer appendix A) after gelation probably

indicating the start of a new reaction within the gel and which strongly controls its conductivity.

Most of these observations above would serve for areas of investigation for further research work.

5.14 Discussion on the kinetics and mechanism of gelation of calcium ligninsulphonate.

Attempts to reveal the mechanism of the gelation by analysing for conductance measurements was unconvincing and it was felt that the conductivity of the gel mixtures is not controlled rigidly by the kinetics of gelation. However the role of metal ion catalysts was successfully investigated with viscosity measurements and interpreted in terms of electron-transfer agents. This in turn requires that the polymerisation is an oxidation-reduction process between the dichromate and ligninsulphonate as opposed to the condensation-dimerisation mechanism advocated by Hayashi.

A problem is thus created in which it is desirable to rationalise the possibility of two different mechanisms purporting to represent the polymerisation process. Hayashi's mechanism is built on a large amount of experimental evidence and exhaustively tested but on the other hand, it is felt that the oxidative process arrived at from this work is all too evident. There is little foundation and rationale to suggest that Hayashi's and the oxidative process are part and parcel of an integrated mechanism and the best recourse appears to be the existance of two different mechanisms productive to polymerisation.

The characteristic feature of the oxidative process is that dichromate would be reduced to chromium(III) and that like any other redox process, is strongly catalysed by suitable electron-transfer agents. In such catalysed mixtures, the oxidative process would be expected to be strongly promoted over Hayashi's mechanism and would permit the occurrence of very rapid gelations. It would also make possible gelation with low molecular weight ligninsulphonate factions as the active sites of gelation are apparently not of pendent catechol groups. The initial step of the catalysed oxidative process definitely involves a complexation between the ligninsulphonate and the catalyst and direct polarographic and spectrometric evidence of the complex formation was obtained.

The hydrogen ions are an essential part of the oxidative process by "promoting" the reduction half-equation of the dichromate ion acting as the oxidant, and they are consumed in large amounts during the polymerisation. They contribute to acceleration simply by their concentration effect and are not catalytic in the category of the heavy metal ions. They have also been shown to aid the catalytic oxidative process by helping the decompositions of strongly formed catalyst-ligninsulphonate complexes which could actually be retarding on the polymerisation. e.g. that with the Fe(III)-ligninsulphonate complex. The hydrogen ions are probably just as much a part of Hayashi's mechanism by serving to control the equilibrium $2CrO_4" + 2H^+ \rightleftharpoons Cr_2O_7" + H_2O$ in which the

$HCrO_4^-$ ion is the active species for formation of the chromate-esters. However additions of hydrochloric acid in fig. 28 indicated that there is no evidence that the optimum pH for gelation is between 3.5 to 4.5[4] and in fact the rate of polymerisation appears to be proportional to decreasing pH except when the molecule is being destroyed (< pH 2.5). The hydrogen ions could also speed up the polymerisation by depressing the negative charges on the liginsulphonate polymer.

CHAPTER VI

SUMMARY

The ligninsulphonate gels catalysed by ferric chloride intended as an electrode grouting by the N.Z.E.D. has been thoroughly studied and their gelling times were found to vary in a complex manner with ligninsulphonate, dichromate and ferric chloride concentrations. A substantial reduction in ligninsulphonate concentration down to 10% solution could be achieved without adversely affecting all other properties other than mechanical strength. A large number of gels defined by the area ABCDE in fig. 18 for 1:1 gel series are recommended as suitable mixtures from which they could be selected to suit the problems demanded of a particular soil condition.

The excess of dichromate in 1:1 gels could be reduced by as much as 50% without adversely affecting the conductivity of the gels. Reduced dichromate concentrations also have the additional advantage of lowering the extent of general oxidation processes and giving more stable gels chemically. However the 1:½ gel series are generally more difficult to form and a substantial reduction short of 50% would be encouraged.

The role of Fe(III) ion in small and moderate concentrations is actually one of a retarder and its presence as a promoter to gelation is redundant. Cu(II) is the most effective

catalyst and much smaller additions are required to produce the same reduction in gelling times. Its salt therefore appears to be an attractive substitute additive for ferric chloride with intent to produce further savings in cost and would also contribute to improvement of the quality and property of the ligninsulphonate gel as permanent ground electrode.

The activity of transition metal salts as promoters in the gelation of ligninsulphonate has been resolved to arise from two contributions (a) the effect of hydrogen ions and (b) the action of the metal aquo ion. The hydrogen ions are shown to be an important reagent in the reaction while the metal ion performed an electron-transfer role. This dissertation is supportive of an oxidative mechanism as the main mechanism for gelation of Discon while Hayashi's mechanism could not be accommodated in any significant role. The stoichiometry of the gelation proved that Hayashi's mechanism is all but impossible.

ACKNOWLEDGEMENT

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Yat Fai Ng November 1976.

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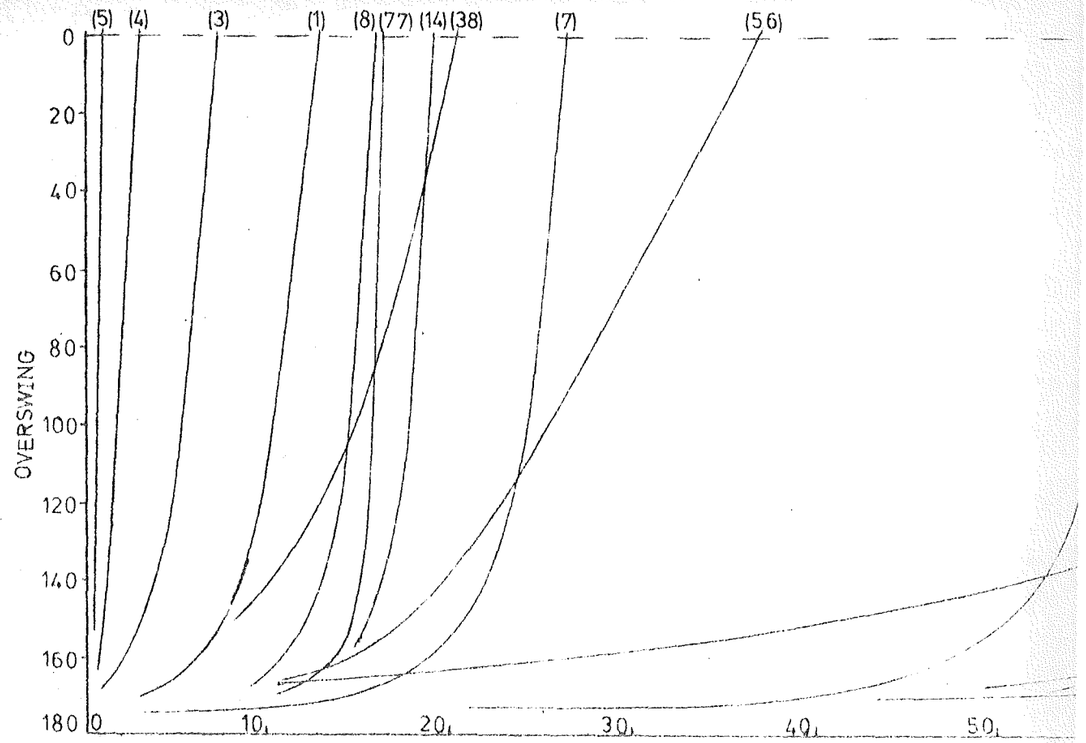
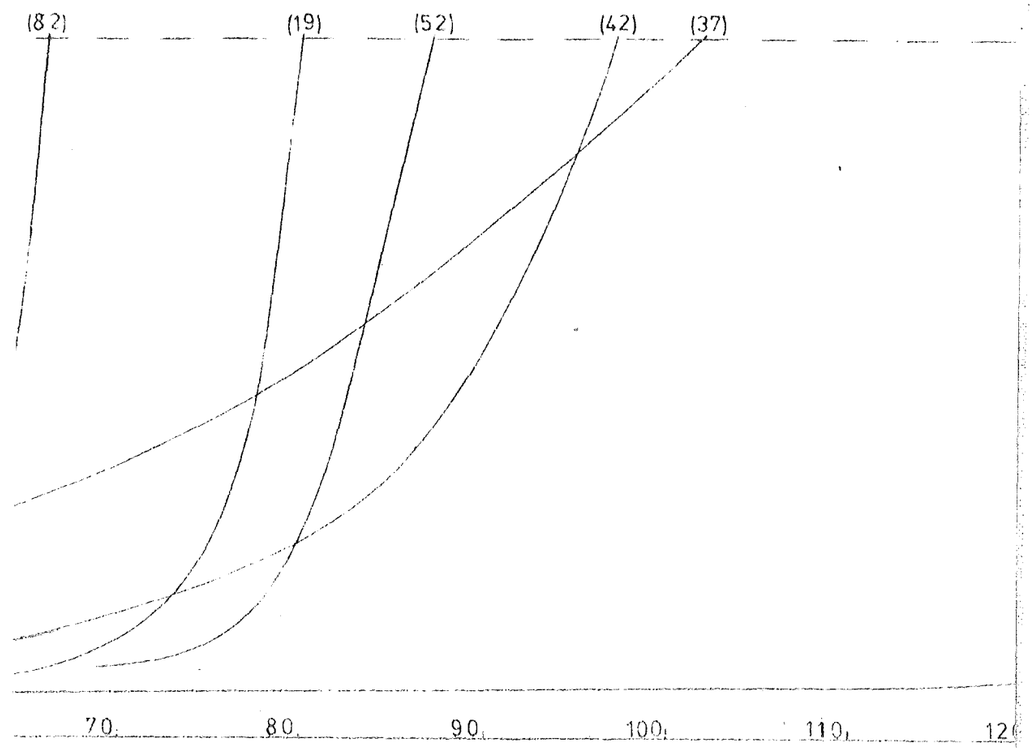
APPENDIX : A

a) VISCOSITY GRAPHS OF >10% LIGNINSULPHONATE GEL MIXTURES. ALL MIXTURE



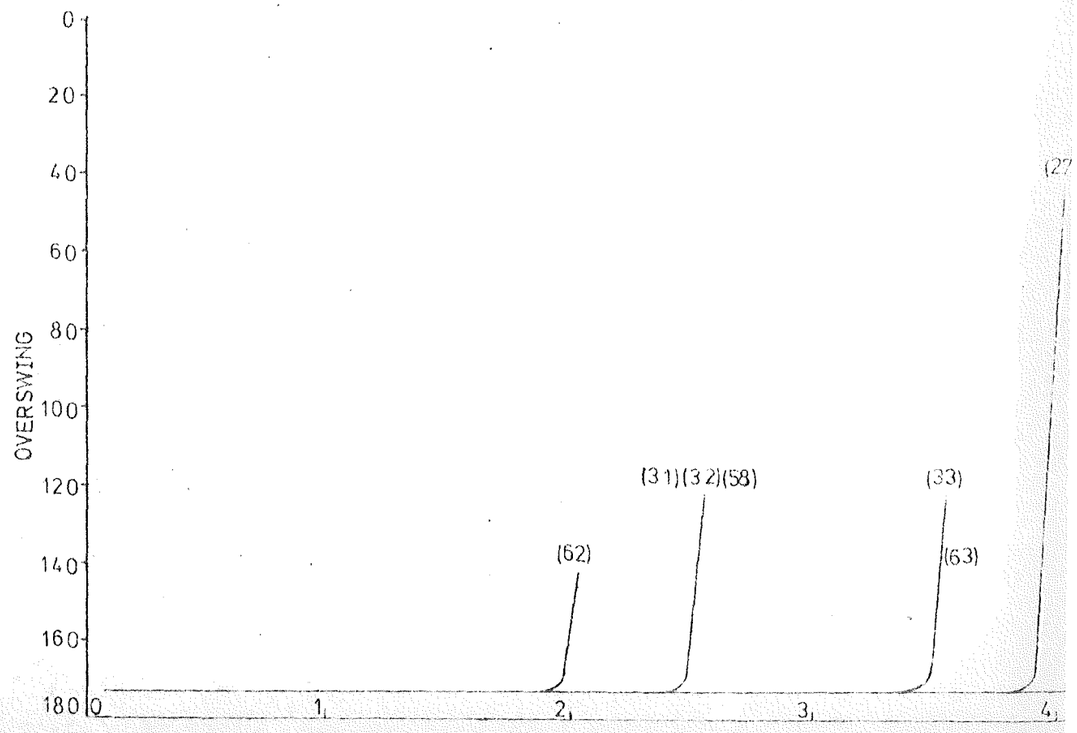
TIME >10 MINUTES REPRESENTED.



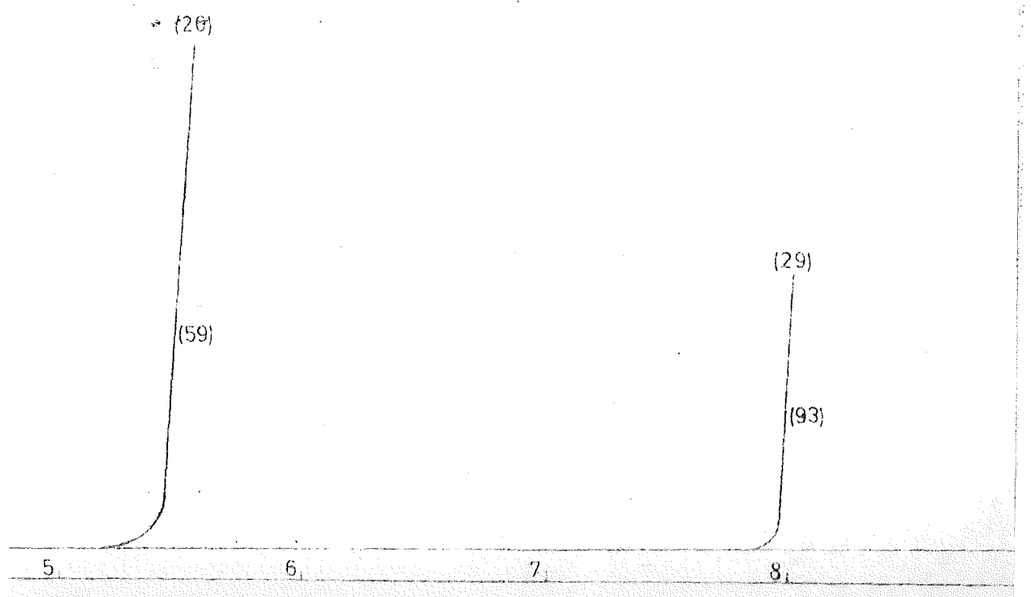
ION TIME IN MINUTES

b) VISCOSITY GRAPHS OF ⩽10% LIGNINSULPHONATE GEL MIXTURES.

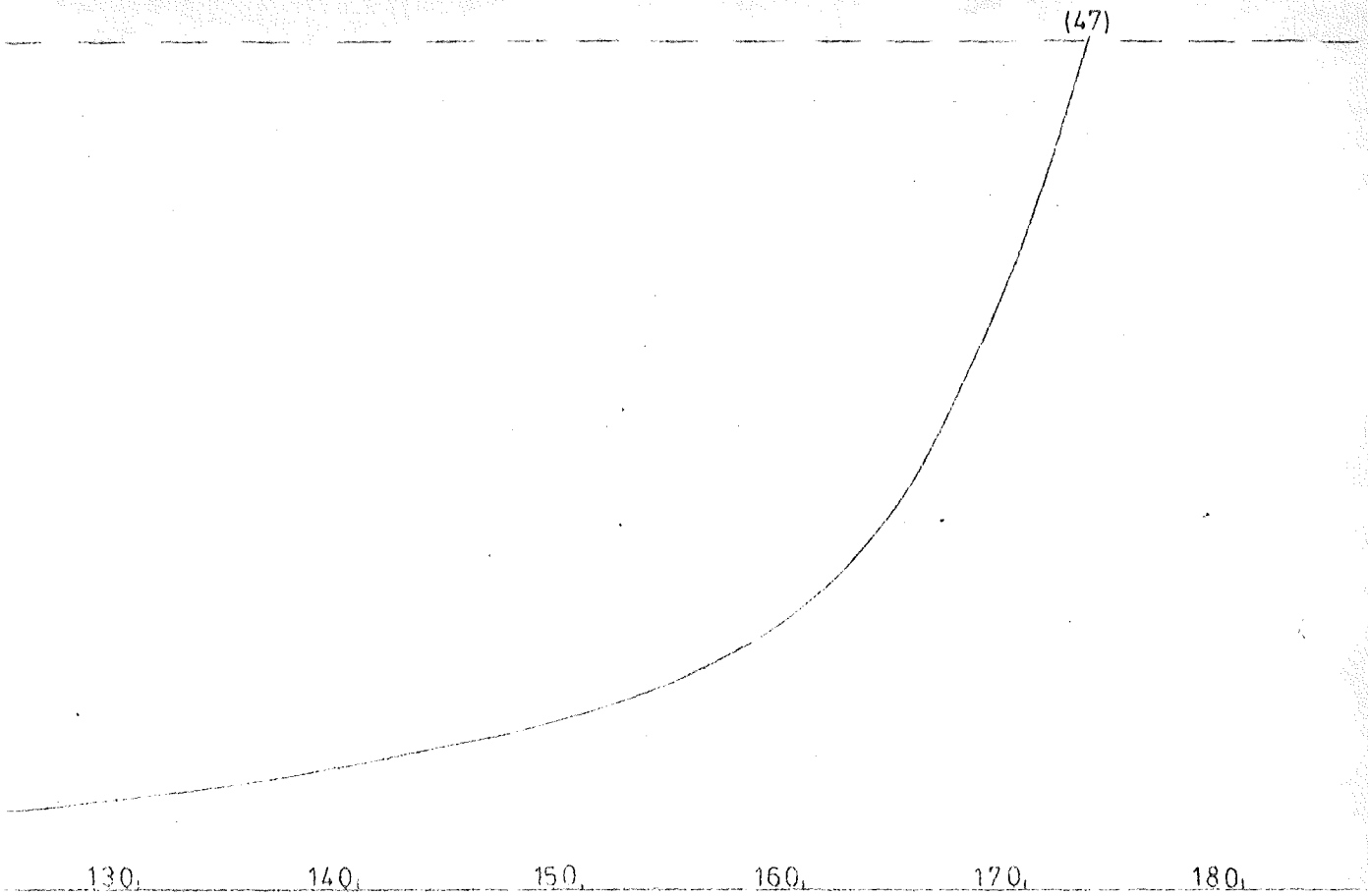
NOTE: VISCOSITY OF GEL FORMED (∝HARDNESS) IS APPROXIMATELY PROP

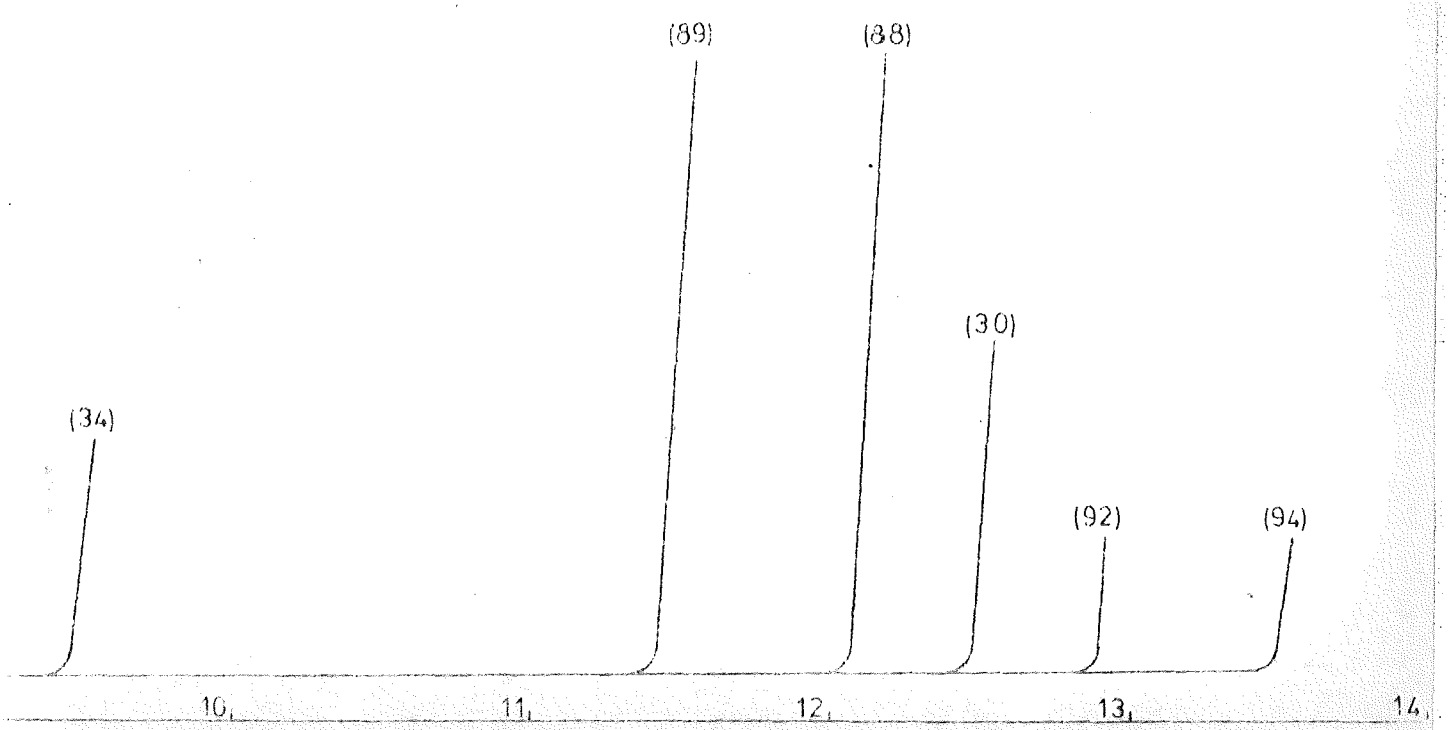


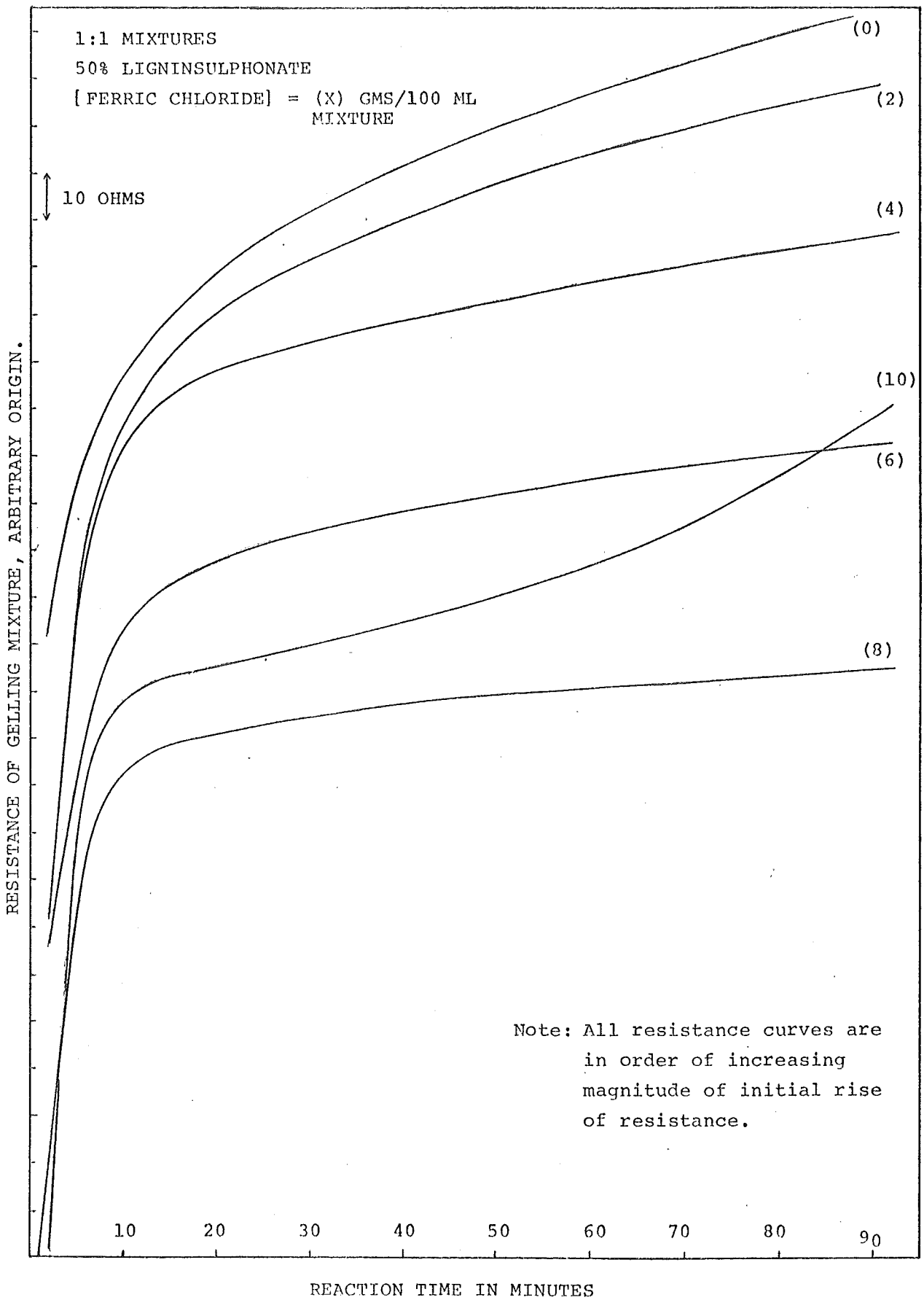
HEIGHT OF CURVES REPRESENTED

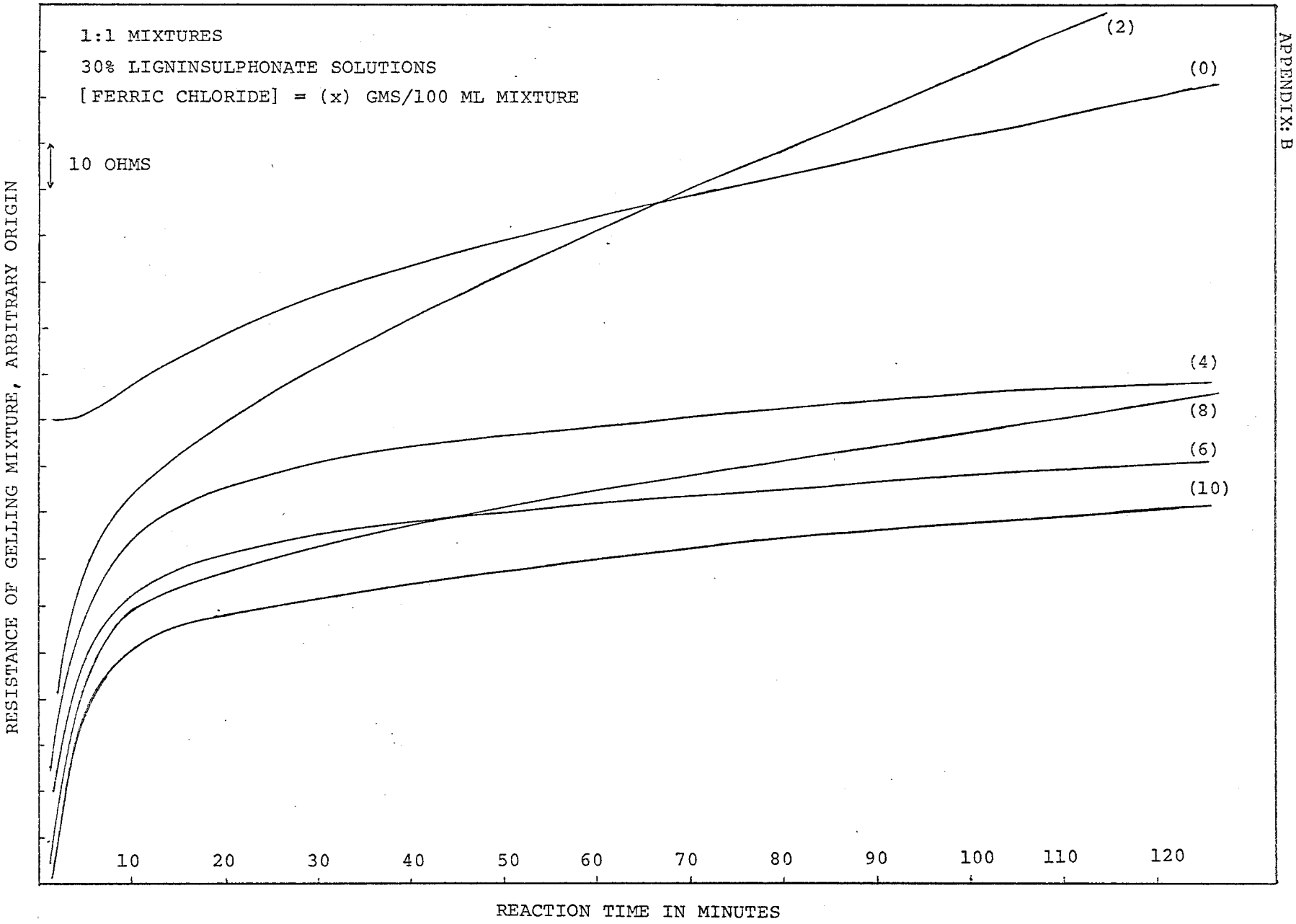


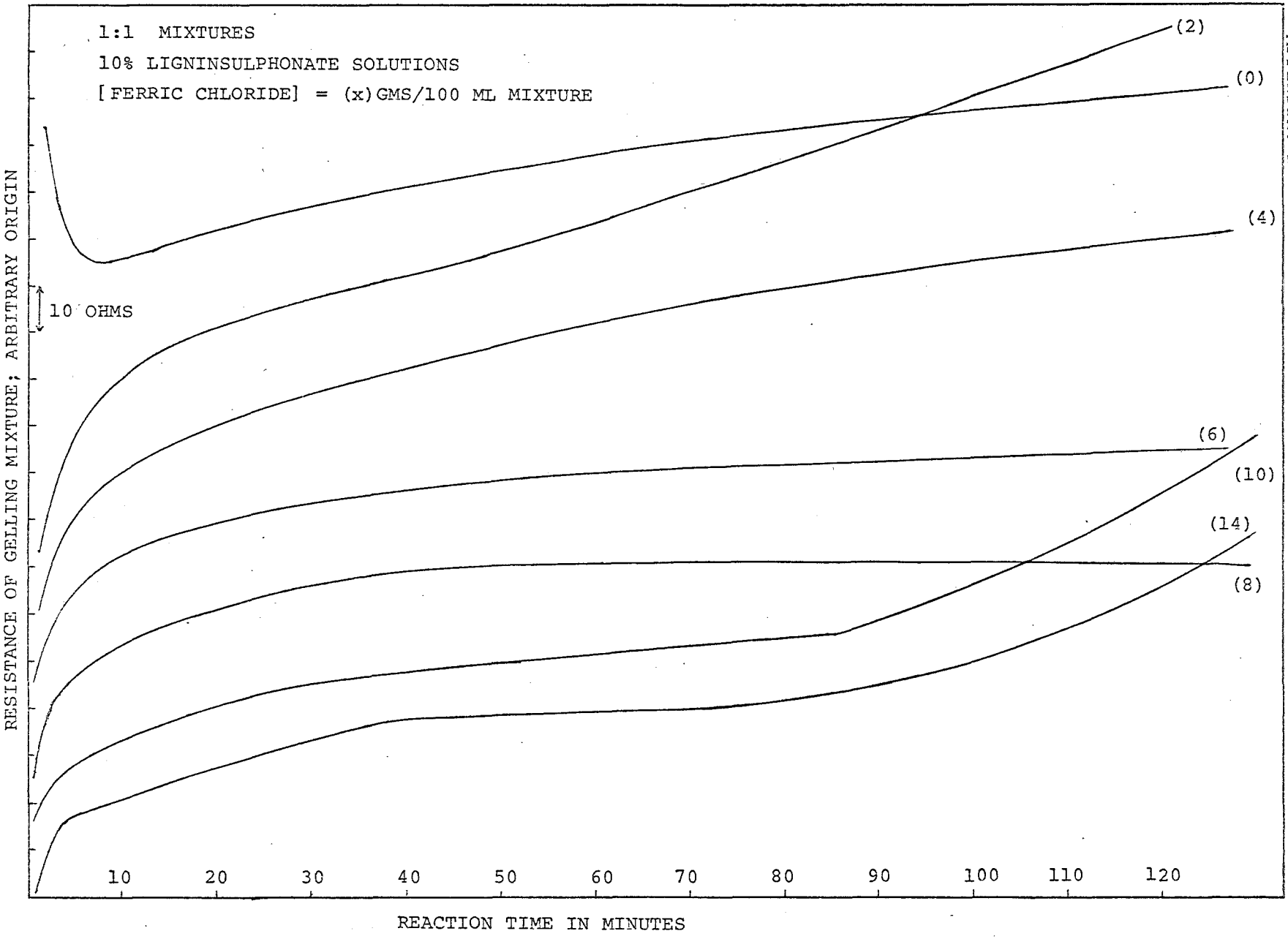
ON TIME IN MINUTES

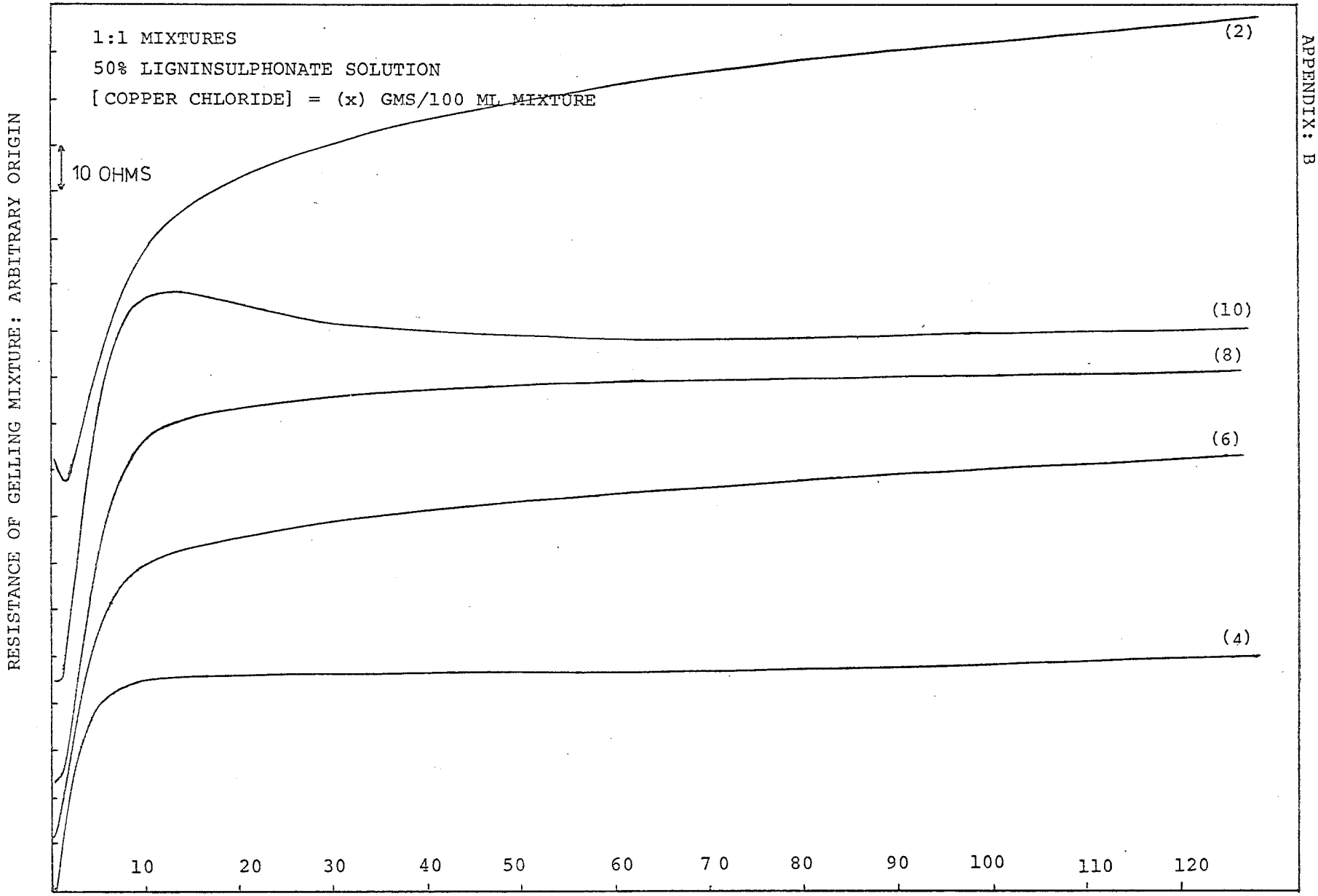

(47)
130
140
150
160
170
180

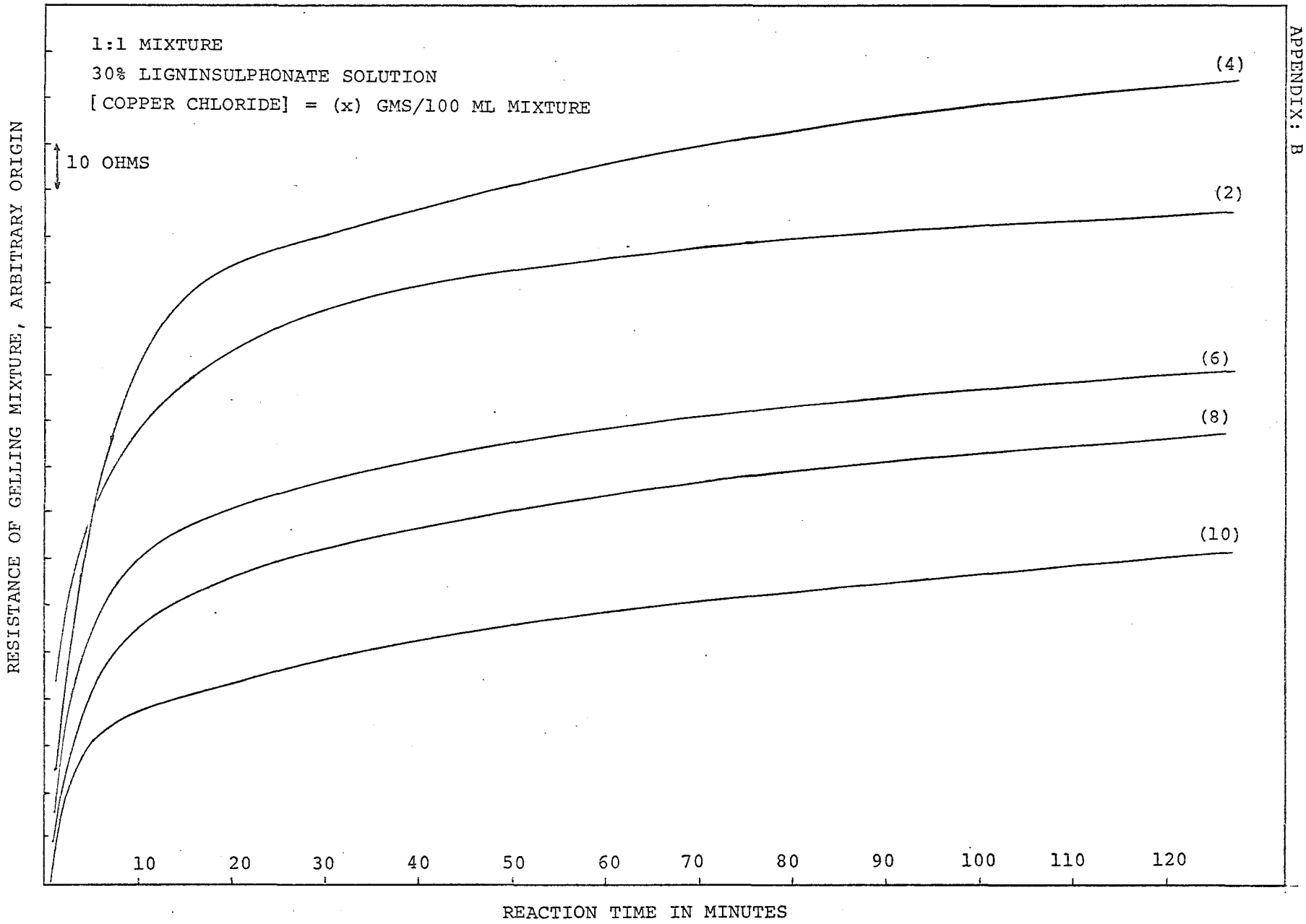

(89)
(88)
(30)
(34)
(92)
(94)
10
11
12
13
14

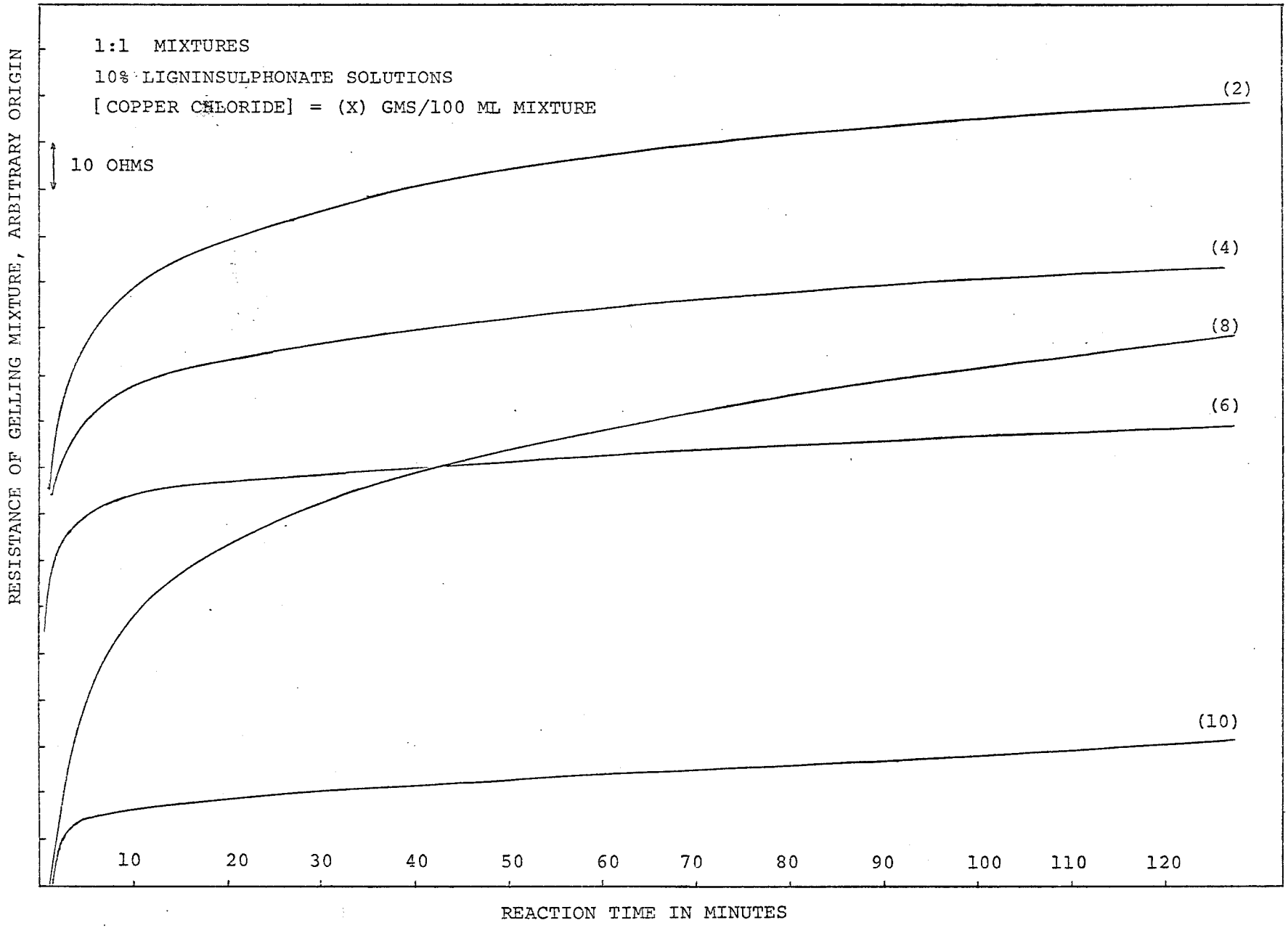

1:1 MIXTURES
50% LIGNINSULPHONATE
[FERRIC CHLORIDE] = (X) GMS/100 ML MIXTURE
10 OHMS
(0)
(2)
(4)
(10)
(6)
(8)
RESISTANCE OF GELLING MIXTURE, ARBITRARY ORIGIN.
Note: All resistance curves are in order of increasing magnitude of initial rise of resistance.
10
20
30
40
50
60
70
80
90
REACTION TIME IN MINUTES

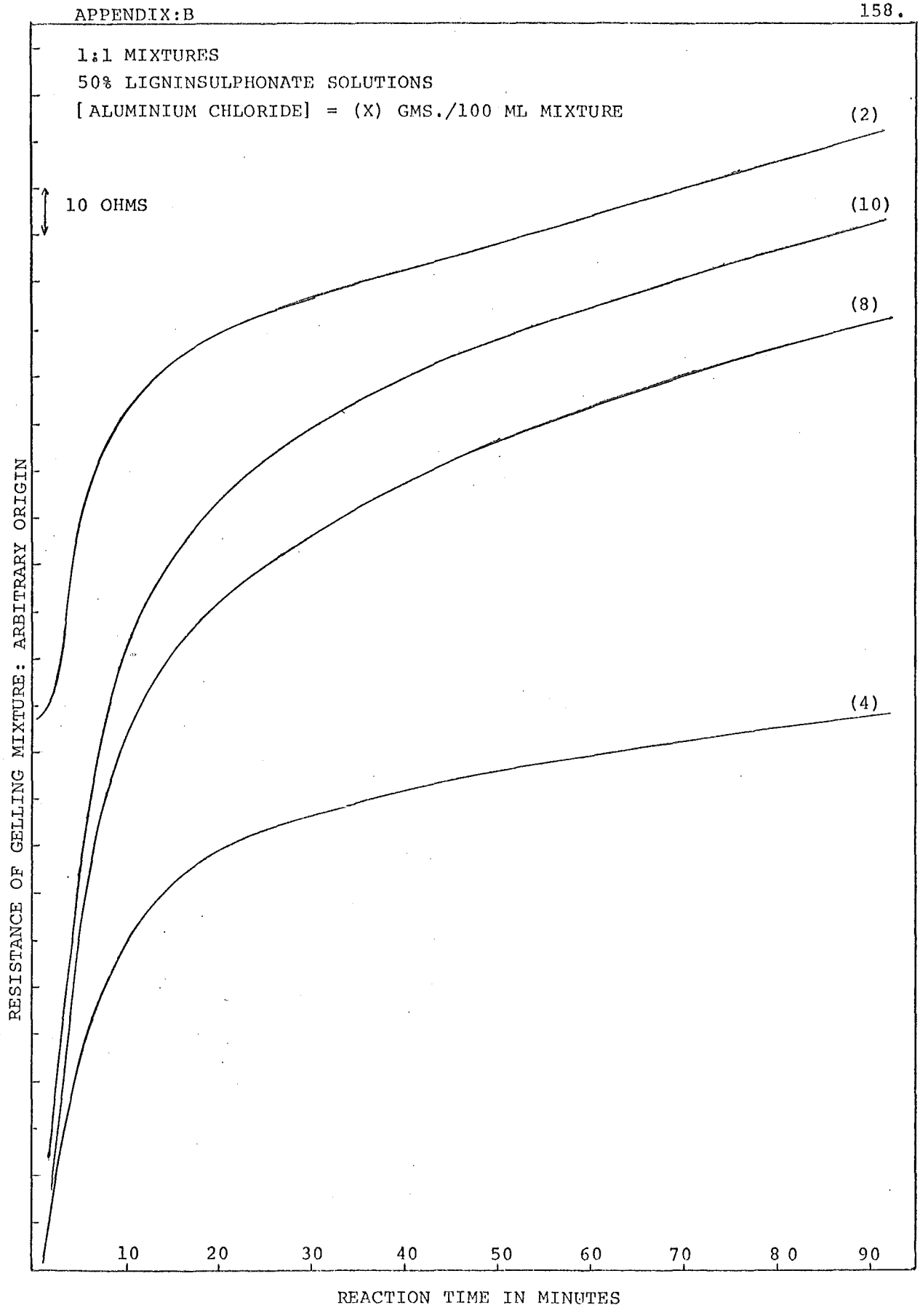

1:1 MIXTURES
30% LIGNINSULPHONATE SOLUTIONS
[FERRIC CHLORIDE] = (x) GMS/100 ML MIXTURE
10 OHMS
(2)
(0)
(4)
(8)
(6)
(10)
RESISTANCE OF GELLING MIXTURE, ARBITRARY ORIGIN
10
20
30
40
50
60
70
80
90
100
110
120
REACTION TIME IN MINUTES


1:1 MIXTURES
10% LIGNINSULPHONATE SOLUTIONS
[FERRIC CHLORIDE] = (x) GMS/100 ML MIXTURE
(2)
(0)
(4)
(6)
(10)
(14)
(8)
10 OHMS
RESISTANCE OF GELLING MIXTURE; ARBITRARY ORIGIN
10
20
30
40
50
60
70
80
90
100
110
120
REACTION TIME IN MINUTES


1:1 MIXTURES
50% LIGNINSULPHONATE SOLUTION
[COPPER CHLORIDE] = (x) GMS/100 ML MIXTURE
10 OHMS
(2)
(10)
(8)
(6)
(4)
RESISTANCE OF GELLING MIXTURE: ARBITRARY ORIGIN
10
20
30
40
50
60
70
80
90
100
110
120
REACTION TIME IN MINUTES


1:1 MIXTURE
30% LIGNINSULPHONATE SOLUTION
[COPPER CHLORIDE] = (x) GMS/100 ML MIXTURE
10 OHMS
(4)
(2)
(6)
(8)
(10)
RESISTANCE OF GELLING MIXTURE, ARBITRARY ORIGIN
10
20
30
40
50
60
70
80
90
100
110
120
REACTION TIME IN MINUTES


1:1 MIXTURES
10% LIGNINSULPHONATE SOLUTIONS
[COPPER CHLORIDE] = (X) GMS/100 ML MIXTURE
10 OHMS
(2)
(4)
(8)
(6)
(10)
10
20
30
40
50
60
70
80
90
100
110
120
RESISTANCE OF GELLING MIXTURE, ARBITRARY ORIGIN
REACTION TIME IN MINUTES


1:1 MIXTURES
50% LIGNINSULPHONATE SOLUTIONS
[ALUMINIUM CHLORIDE] = (X) GMS./100 ML MIXTURE
(2)
10 OHMS
(10)
(8)
(4)
RESISTANCE OF GELLING MIXTURE: ARBITRARY ORIGIN
10
20
30
40
50
60
70
80
90
REACTION TIME IN MINUTES

APPENDIX: C

TABLE 11: Evolution of heat in a 46.6 ml ligninsulphonate gel mixture (1:1 ratio) promoted by chloride additives.

(a)

Moles of hydrochloric acid	Gelling Time (mins.)	Quantity of heat evolved
0.0000	29.00	Little heat evolved
0.0104	14.50	Little heat evolved
0.0208	5.40	Increased heat evolved
0.0312	3.38	Increased heat evolved
0.0416	2.50	Quite large heat evolved
0.0520	2.95	Quite large heat evolved
0.0624	3.18	Quite large heat evolved
0.0832	5.25	Large heat evolved
0.1040	31.00	Large heat evolved

(b)

Moles of aluminium chloride	Gelling Time (mins.)	Quantity of heat evolved
0.00346	17.35	
0.00749	11.50	
0.01042	8.85	No heat evolved at all
0.01386	9.00	Reaction mixture remained
0.01733	7.00	cold throughout
0.02079	7.30	
0.02773	6.80	
0.03467	6.20	

(c)

Moles of ferric chloride	Gelling Time (mins.)	Quantity of heat evolved
0.00346	26.25	No heat evolved
0.00694	8.25	Little heat evolved
0.01039	1.50	Some heat evolved
0.01386	<0.50	Some heat evolved
0.01733	<0.30	Moderate heat evolved

(d)

Moles of cupric chloride	Gelling Time (mins.)	Quantity of heat evolved
0.00520	2.25	No heat evolved
0.01039	0.50	No heat evolved
0.01559	0.30	A little heat evolved

(e)

Moles of manganous chloride	Gelling Time (mins.)	Quantity of heat evolved
0.00260	10.95	
0.00779	5.85	
0.01298	4.30	
0.01559	3.90	Cold reaction
0.01820	3.78	
0.02339	3.23	
0.02859	2.85	

(f)

Moles of chromium chloride	Gelling Time (mins.)	Quantity of heat evolved
0.00347	22.50	No heat evolved
0.00693	13.80	No heat evolved
0.01039	11.45	No heat evolved
0.01386	9.90	little heat evolved
0.01733	8.80	little heat evolved
0.02079	9.55	little heat evolved